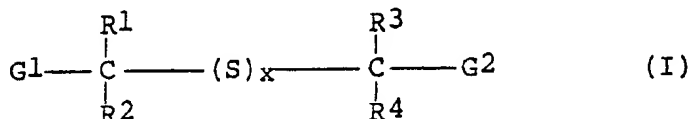




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(54) Title: COMPOSITIONS AND LUBRICANTS AND FUNCTIONAL FLUIDS CONTAINING SAME



**(57) Abstract**

A composition is disclosed which comprises: (A) at least one neutral or basic metal salt or boron-containing neutral or basic metal salt of at least one acidic organic compound, the metal in said salt being selected from the group consisting of alkali metals, alkaline-earth metals, zinc, copper, aluminum or a mixture of two or more of said metals; (B) at least one metal deactivator; and (C) at least one compound selected from the group consisting of (C-1) phosphorus-containing amide; (C-2) phosphorus-containing ester; (C-3) sulfur-coupled dithiocarbamate; (C-4) sulfur-containing compound represented by the formula (I), wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are each independently H or hydrocarbyl groups,  $R^1$  and/or  $R^3$  may be  $G^1$  or  $G^2$ ;  $R^1$  and  $R^2$  and/or  $R^3$  and  $R^4$  together may be alkylene groups containing about 4 to about 7 carbon atoms;  $G^1$  and  $G^2$  are each independently  $C(X)R$ ,  $COOR$ ,  $C \equiv N$ ,  $R^5-C=NR^6$ ,  $CON(R)_2$  or  $NO_2$ , and  $G^1$  also may be  $CH_2OH$ , wherein X is O or S, each of R and  $R^5$  are independently H or a hydrocarbyl group,  $R^6$  is H or a hydrocarbyl group; when both  $G^1$  and  $G^2$  are  $R^5-C=NR^6$ , the two  $R^6$  groups together may be a hydrocarbylene group linking the two nitrogen atoms; when  $G^1$  is  $CH_2OH$  and  $G^2$  is  $COOR$ , a lactone may be formed by intramolecular condensation of  $G^1$  and  $G^2$ ; and x is an integer from 1 to about 8; and (C-5) mixture of two or more of any of (C-1) to (C-4). These compositions are useful as additives for lubricants and functional fluids, particularly hydraulic fluids, gear oils, greases and the like.

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COMPOSITIONS AND LUBRICANTS AND FUNCTIONAL  
FLUIDS CONTAINING SAME

Technical Field

This invention relates to compositions comprising (A) at least one neutral or basic metal salt or boron-containing neutral or basic metal salt of at least one acidic organic compound, (B) at least one metal deactivator, and (C) at least one sulfur- and/or phosphorus-containing compound. These compositions are useful in providing lubricants and functional fluids with thermal stability and improved anti-wear, extreme-pressure, load-carrying and/or corrosion-inhibiting properties.

Background of the Invention

Zinc-containing hydraulic fluids are widely accepted for numerous applications. These hydraulic fluids typically have excellent thermal stability and anti-wear properties due to the use therein of zinc-containing anti-wear agents. In recent years, however, there has been a growing concern about the accumulation in the workplace and environment of heavy metals such as zinc. This concern has led to a demand for hydraulic fluids containing ashless anti-wear agents. Ashless anti-wear agents are available, but hydraulic fluids based thereon typically lack sufficient thermal stability to be acceptable for many uses.

The book "Lubricant Additives" by M.W. Ranney, published by Noyes Data Corporation of Parkridge, N.J. (1973), discloses a number of metal salts of various

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sulfonic and carboxylic acids and of phenols which are useful as detergent/dispersants in lubricating oil products. The book also entitled "Lubricant Additives" by C.V. Smallheer and R.K. Smith, published by the Lezius-Hiles Co. of Cleveland, Ohio (1967), similarly disclosed a number of detergent/dispersants including sulfonates, phenates and carboxylates which are useful as dispersants. U.S. Patent 4,100,082 discloses the use of neutral or basic metal salts of organic sulfur acids, carboxylic acids and phenols as detergent/dispersants for use in fuels and lubricants.

U.S. Patent 4,627,928 discloses the use of basic magnesium salts of substituted aromatic hydroxy carboxylic acids as dispersants, detergents, antioxidants, etc., for lubricants and fuels.

The use of triazoles such as benzotriazole as metal deactivators in lubricant compositions is disclosed in U.S. Patents 3,413,227; 4,162,225; 4,174,285; and 4,187,186.

The use of phosphorus-containing amides as anti-wear agents for use in lubricant compositions is disclosed in U.S. Patents 4,032,461; 4,208,357; 4,282,171; and 4,670,169.

The use of phosphorus-containing esters as anti-wear agents for use in lubricating compositions is disclosed in U.S. Patent 3,359,203. The use of such esters as E.P. agents in lubricant compositions is disclosed in U.K. Patent 1,347,845.

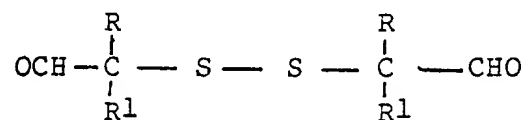
Compositions prepared by the sulfurization of various organic materials including olefins are known in the art, and lubricants containing these compositions also are known. U.S. Patent 4,191,659 describes the preparation of sulfurized olefinic compounds by the

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catalytic reaction of sulfur and hydrogen sulfide with olefinic compounds containing from 3 to 30 carbon atoms. The compounds are reported to be useful in lubricating compositions, particularly those prepared for use as industrial gear lubricants. U.S. Patent 4,119,549 describes a similar procedure for sulfurizing olefins utilizing sulfur and hydrogen sulfide followed by removal of low boiling materials from said sulfurized mixture.

Sulfur-containing compositions characterized by the presence of at least one cycloaliphatic group with at least two nuclear carbon atoms of one cycloaliphatic group or two nuclear carbon atoms of different cycloaliphatic groups joined together through a divalent sulfur linkage are described in Reissue Patent Re 27,331. The sulfur linkage contains at least two sulfur atoms, and sulfurized Diels-Alder adducts are illustrative of the compositions disclosed in the reissue patent. The sulfur-containing compositions are useful as extreme pressure and anti-wear additives in various lubricating oils.

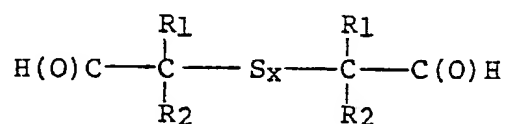
Dialdehydes containing disulfide groups and represented by the formula



wherein both R groups are the same alkyl groups of 1 to 18 carbon atoms and both Rl groups are the same alkyl or aryl groups are described in U.S. Patent 2,580,695. The compounds are reported to be useful as cross-linking agents and as chemical intermediates.

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Lubricating compositions containing sulfides having the formula



wherein R<sub>1</sub> is a hydrocarbon group, R<sub>2</sub> is hydrogen or a hydrocarbon group, and x is 1 to 2 are described in U.S. Patent 3,296,137.

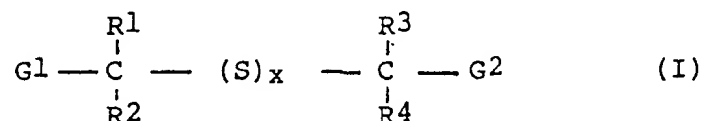
Canadian Patent 1,168,222 discloses the use as additives for lubricants the combination of (A) at least one benzotriazole or the reaction product of a benzotriazole with at least one aliphatic amine, and (B) at least one sulfurized aliphatic or alicyclic compound containing about 3-30 carbon atoms. This patent indicates that the lubricants can also contain ash-producing detergents exemplified by oil-soluble neutral and basic salts of alkali and alkaline earth metals with sulfonic acids, carboxylic acids or organic phosphorus acids.

#### Summary of the Invention

This invention provides for a composition comprising: (A) at least one neutral or basic metal salt or boron-containing neutral or basic metal salt of at least one acidic organic compound, the metal in said salt being selected from the group consisting of alkali metals, alkaline-earth metals, zinc, copper, aluminum or a mixture of two or more of said metals; (B) at least one metal deactivator; and (C) at least one compound selected from the group consisting of (C-1) phosphorus-containing amide; (C-2) phosphorus-containing ester;

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(C-3) sulfur-coupled dithiocarbamate; (C-4) sulfur-containing compound represented by the formula



wherein in Formula I: R1, R2, R3 and R4 are each independently H or hydrocarbyl groups; R1 and/or R3 may be G1 or G2; R1 and R2 and/or R3 and R4 together may be alkylene groups containing about 4 to about 7 carbon atoms; G1 and G2 are each independently C(X)R, COOR, C≡N, R<sup>5</sup>-C=NR<sup>6</sup>, CON(R)<sub>2</sub> or NO<sub>2</sub>, and G1 also may be CH<sub>2</sub>OH, wherein X is O or S, each of R and R<sup>5</sup> are independently H or a hydrocarbyl group, R<sup>6</sup> is H or a hydrocarbyl group; when both G1 and G2 are R<sup>5</sup>C=NR<sup>6</sup>, the two R<sup>6</sup> groups together may be a hydrocarbylene group linking the two nitrogen atoms; when G1 is CH<sub>2</sub>OH and G2 is COOR, a lactone may be formed by intramolecular condensation of G1 and G2; and x is an integer from 1 to about 8; and (C-5) mixture of two or more of any of (C-1) to (C-4). These compositions are useful as additives for lubricants and functional fluids, particularly hydraulic fluids, gear oils, greases and the like.

#### Description of the Preferred Embodiments

As used in this specification and in the appended claims, the term "hydrocarbyl" denotes a group having a carbon atom directly attached to the remainder of the molecule and having a hydrocarbon or predominantly hydrocarbon character within the context of this invention. Such groups include the following:

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(1) Hydrocarbon groups; that is, aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic groups, and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic group). Such groups are known to those skilled in the art. Examples include methyl, ethyl, octyl, decyl, octadecyl, cyclohexyl, phenyl, etc.

(2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of suitable substituents. Examples include halo, hydroxy, nitro, cyano, alkoxy, acyl, etc.

(3) Hetero groups; that is, groups which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and preferably no more than one, will be present for each 10 carbon atoms in the hydrocarbon group.

Terms such as "alkyl-based", "aryl-based", and the like have meanings analogous to the above with respect to alkyl groups, aryl groups and the like.

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The term "hydrocarbon-based" has the same meaning and can be used interchangeably with the term hydrocarbyl when referring to molecular groups having a carbon atom attached directly to the remainder of a molecule.

The term "lower" as used herein in conjunction with terms such as hydrocarbyl, alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms.

The term "oil-soluble" refers to a material that is soluble in mineral oil to the extent of at least about one gram per liter at 25°C.

Component (A):

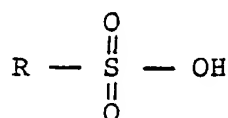
Component (A) is a neutral or basic metal salt or boron-containing neutral or basic metal salt of at least one acidic organic compound, the metal in said salt being selected from the group consisting of alkali metals, alkaline-earth metals, zinc, copper, aluminum or a mixture of two or more of said metals.

The acidic organic compound from which these salts are derived can be one or more carboxylic acids, sulfur-containing acids, phosphorus-containing acids, phenols, or a mixture of two or more thereof. These acidic organic compounds are discussed in greater detail below.

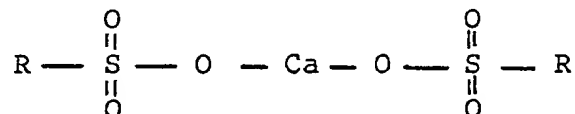
The term "basic" is a term of art which is generic to well known classes of metal salts. These basic metal salts have also been referred to as "overbased", "superbased", "hyperbased", "high-metal containing salts", and the like. Basic metal salts are characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular acidic organic compound reacted with the

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metal, e.g., a sulfonic acid. Thus, if a monosulfonic acid,



is neutralized with a basic metal compound, e.g., calcium hydroxide, the "neutral" or "normal" metal salt produced will contain one equivalent of calcium for each equivalent of acid, i.e.,



Processes for making such neutral and basic metal salts are well known in the art. Neutral salts can be made by heating a mineral oil solution of an acidic organic compound with a stoichiometric equivalent amount of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature above about 50°C and filtering the resulting mass. Basic salts are similarly made with the exception that a stoichiometric excess of the metal is used. Also, a "promoter" in the neutralization step to aid the incorporation of the excess metal can be used in making the basic salts. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, cellosolve, carbitol, ethylene glycol,

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stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-beta-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing the acid organic compound with an excess of a basic metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60-200°C.

Component (A) typically has from about 100% to about 4000%, preferably from about 100% to about 3000%, more preferably from about 100% to about 2800%, more preferably from about 200% to about 1000% of the metal present in the corresponding neutral salt. In an advantageous embodiment, component (A) has from about 110% to about 4000%, preferably from about 110% to about 3000%, more preferably from about 110% to about 2800%, more preferably from about 110% to about 1000% of the metal present in the corresponding neutral salt.

Preferred metals for the salts (A) include lithium, sodium, magnesium, calcium, potassium, barium, aluminum, zinc and copper. Mixtures of two or more of the foregoing metals can be used. Particularly preferred metals are sodium, magnesium, calcium or mixtures of two or more thereof.

#### Carboxylic Acids:

The carboxylic acids useful in making the salts (A) of the invention may be aliphatic or aromatic, mono- or polycarboxylic acid or acid-producing compounds. These carboxylic acids include lower molecular weight carboxylic acids (e.g., carboxylic acids having up to about 18 carbon atoms such as fatty acids having about 10 to about 18 carbon atoms or tetrapropenyl-substituted succinic anhydride) as well as higher molecular weight

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carboxylic acids. Throughout this specification and in the appended claims, any reference to carboxylic acids is intended to include the acid-producing derivatives thereof such as anhydrides, esters, acyl halides, lactones and mixtures thereof unless otherwise specifically stated.

The carboxylic acids of this invention are preferably oil-soluble and the number of carbon atoms present in the acid is important in contributing to the desired solubility of the salts (A). Usually, in order to provide the desired oil-solubility, the number of carbon atoms in the carboxylic acid should be at least about 8 carbon atoms, more preferably at least about 18 carbon atoms, more preferably at least about 30 carbon atoms, more preferably at least about 50 carbon atoms. Generally, these carboxylic acids do not contain more than about 400 carbon atoms per molecule.

The carboxylic acid may contain polar substituents provided that the polar substituents are not present in portions sufficiently large to alter significantly the hydrocarbon character of the carboxylic acid. Typical suitable polar substituents include halo, such as chloro and bromo, oxo, oxy, formyl, sulfenyl, sulfinyl, thio, nitro, etc. Such polar substituents, if present, preferably do not exceed about 10% by weight of the total weight of the hydrocarbon portion of the carboxylic acid, exclusive of the carboxyl groups.

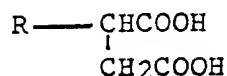
The lower molecular weight monocarboxylic acids contemplated for use in this invention include saturated and unsaturated acids. Examples of such useful acids include dodecanoic acid, palmitic acid, decanoic acid, oleic acid, lauric acid, stearic acid, myristic acid, linoleic acid, linolenic acid, naphthenic acid, chloro-

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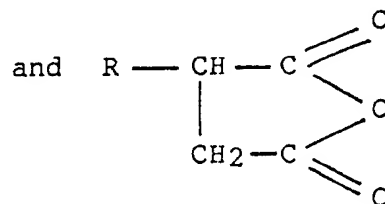
stearic acid, tall oil acid, etc. Anhydrides and lower alkyl esters of these acids can also be used. Mixtures of two or more such agents can also be used. An extensive discussion of these acids is found in Kirk-Othmer "Encyclopedia of Chemical Technology" Third Edition, 1978, John Wiley & Sons New York, pp. 814-871; these pages being incorporated herein by reference.

Examples of lower molecular weight polycarboxylic acids include dicarboxylic acids and derivatives such as sebacic acid, cetyl malonic acid, tetrapropylene-substituted succinic anhydride, etc. Lower alkyl esters of these acids can also be used.

Lower molecular weight hydrocarbyl-substituted succinic acids and anhydrides can also be used. Typically, these compounds are represented, respectfully, by the formulae



(II)



(III)

wherein in Formulae II and III, R is a hydrocarbyl group of from about 8 to about 18 carbon atoms. Preferably, R is an aliphatic or alicyclic hydrocarbyl group with less than 10% of its carbon-to-carbon bonds being unsaturated. Examples of such groups include 4-butylcyclohexyl, di(isobutyl), decyl, etc. The production of such substituted succinic acids and their derivatives via alkylation of maleic acid or its derivatives with a halohydro-

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carbon is well known to those of skill in the art and need not be discussed in detail herein.

Acid halides of the afore-described lower molecular weight mono- and polycarboxylic acids can be used as lower molecular weight carboxylic acids in this invention. These can be prepared by the reaction of such acids or their anhydrides with halogenating agents such as phosphorus tribromide, phosphorus pentachloride, phosphorus oxychloride or thionyl chloride. Esters of such acids can be prepared simply by the reaction of the acid, acid halide or anhydride with an alcohol or phenolic compound. Particularly useful are the lower alkyl and alkenyl alcohols such as methanol, ethanol, allyl alcohol, propanol, cyclohexanol, etc. Esterification reactions are usually promoted by the use of alkaline catalysts such as sodium hydroxide or alkoxide, or an acidic catalyst such as sulfuric acid or toluene sulfonic acid.

The monocarboxylic acids include isoaliphatic acids, i.e., acids having one or more lower acyclic pendant alkyl groups. Such acids often contain a principal chain having from about 14 to about 20 saturated, aliphatic carbon atoms and at least one but usually no more than about four pendant acyclic alkyl groups. The principal chain of the acid is exemplified by groups derived from tetradecane, pentadecane, hexadecane, heptadecane, octadecane, and eicosane. The pendant group is preferably a lower alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-hexyl, or other groups having up to about 7 carbon atoms. The pendant group may also be a polar-substituted alkyl group such as chloromethyl, bromobutyl, methoxyethyl, or the like, but it preferably contains no more

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than one polar substituent per group. Specific examples of such isoaliphatic acids include 10-methyl-tetradecanoic acid, 11-methyl-pentadecanoic acid, 3-ethyl-hexadecanoic acid, 15-methyl-heptadecanoic acid, 16-methyl-heptadecanoic acid, 6-methyl-octadecanoic acid, 8-methyl-octadecanoic acid, 10-methyl-octadecanoic acid, 14-methyl-octadecanoic acid, 16-methyl-octadecanoic acid, 15-ethyl-heptadecanoic acid, 3-chloromethyl-nonadecanoic acid, 7,8,9,10-tetramethyl-octadecanoic acid, and 2,9,10-trimethyl-octadecanoic acid.

The isoaliphatic acids include mixtures of branch-chain acids prepared by the isomerization of commercial fatty acids of, for example, about 16 to about 20 carbon atoms. A useful method involves heating the fatty acid at a temperature above about 250°C and a pressure between about 200 and 700 psi, distilling the crude isomerized acid, and hydrogenating the distillate to produce a substantially saturated isomerized acid. The isomerization can be promoted by a catalyst such as mineral clay, diatomaceous earth, aluminum chloride, zinc chloride, ferric chloride, or some other Friedel-Crafts catalyst. The concentration of the catalyst may be as low as about 0.01%, but more often from about 0.1% to about 3% by weight of the isomerization mixture. Water also promotes the isomerization and a small amount, from about 0.1% to about 5% by weight, of water may thus be advantageously added to the isomerization mixture. The unsaturated fatty acids from which the isoaliphatic acids may be derived include oleic acid, linoleic acid, linolenic acid, and commercial fatty acid mixtures such as tall oil acids.

The higher molecular weight mono- and polycarboxylic acids suitable for use in making the salts (A)

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are well known in the art and have been described in detail, for example, in the following U.S., British and Canadian patents: U.S. Patents 3,024,237; 3,087,936; 3,163,603; 3,172,892; 3,215,707; 3,219,666; 3,231,587; 3,245,910; 3,254,025; 3,271,310; 3,272,743; 3,272,746; 3,278,550; 3,288,714; 3,306,907; 3,307,928; 3,312,619; 3,341,542; 3,346,354; 3,367,943; 3,373,111; 3,374,174; 3,381,022; 3,394,179; 3,454,607; 3,346,354; 3,470,098; 3,630,902; 3,652,616; 3,755,169; 3,868,330; 3,912,764; 4,234,435; and 4,368,133; British Patents 944,136; 1,085,903; 1,162,436; and 1,440,219; and Canadian Patent 956,397. These patents are incorporated herein by reference.

As disclosed in the foregoing patents, there are several processes for preparing these higher molecular weight carboxylic acids. Generally, these processes involve the reaction of (1) an ethylenically unsaturated carboxylic acid, acid halide, anhydride or ester reactant with (2) an ethylenically unsaturated hydrocarbon containing at least about 18 aliphatic carbon atoms or a chlorinated hydrocarbon containing at least about 18 aliphatic carbon atoms at a temperature within the range of about 100-300°C. The chlorinated hydrocarbon or ethylenically unsaturated hydrocarbon reactant preferably contains at least about 20 carbon atoms, more preferably at least about 30 carbon atoms, more preferably at least about 40 carbon atoms, more preferably at least about 50 carbon atoms, and may contain polar substituents, oil-solubilizing pendant groups, and be unsaturated within the general limitations explained hereinabove. It is these hydrocarbon reactants which provide most of the aliphatic carbon atoms present in the acyl moiety of the final products.

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When preparing the higher molecular weight carboxylic acids, the carboxylic acid reactant usually corresponds to the formula  $R_0-(COOH)_n$ , where  $R_0$  is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond and  $n$  is an integer from 1 to about 6 and preferably 1 or 2. The acidic reactant can also be the corresponding carboxylic acid halide, anhydride or ester. Ordinarily, the total number of carbon atoms in the acidic reactant will not exceed about 20, preferably this number will not exceed about 10 and generally will not exceed about 6. Preferably the acidic reactant will have at least one ethylenic linkage in an alpha, beta-position with respect to at least one carboxyl function. Exemplary acidic reactants are acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, glutaconic acid, chloromaleic acid, aconitic acid, crotonic acid, methylcrotonic acid, sorbic acid, 3-hexenoic acid, 10-decenoic acid, and the like. Preferred acid reactants include acrylic acid, methacrylic acid, maleic acid, and maleic anhydride.

The ethylenically unsaturated hydrocarbon reactant and the chlorinated hydrocarbon reactant used in the preparation of these higher molecular weight carboxylic acids are preferably high molecular weight, substantially saturated petroleum fractions and substantially saturated olefin polymers and the corresponding chlorinated products. Polymers and chlorinated polymers derived from mono-olefins having from 2 to about 30 carbon atoms are preferred. Especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-hep-

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tene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. These are exemplified by 2-butene, 3-pentene, and 4-octene.

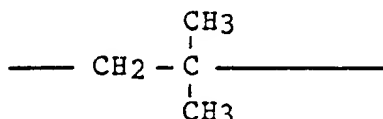
Interpolymers of 1-mono-olefins such as illustrated above with each other and with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins, are also useful sources of the ethylenically unsaturated reactant. Such interpolymers include for example, those prepared by polymerizing isobutene with styrene, isobutene with butadiene, propene with isoprene, propene with isobutene, ethylene with piperylene, isobutene with chloroprene, isobutene with p-methyl-styrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl-1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene, isobutene with styrene and piperylene, etc.

For reasons of oil solubility, the interpolymers contemplated for use in preparing the carboxylic acids of this invention are preferably substantially aliphatic and substantially saturated, that is, they should contain at least about 80% and preferably about 95%, on a weight basis, of units derived from aliphatic mono-olefins. Preferably, they will contain no more than about 5% olefinic linkages based on the total number of the carbon-to-carbon covalent linkages present.

In one embodiment of the invention, the polymers and chlorinated polymers are obtained by the polymerization of a C4 refinery stream having a butene content of about 35% to about 75% by weight and an isobutene content of about 30% to about 60% by weight in the presence of a Lewis acid catalyst such as aluminum

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chloride or boron trifluoride. These polyisobutenes preferably contain predominantly (that is, greater than about 80% of the total repeat units) isobutene repeat units of the configuration.



The chlorinated hydrocarbons and ethylenically unsaturated hydrocarbons used in the preparation of the higher molecular weight carboxylic acids can have number average molecular weights of up to about 100,000 or even higher, although preferred higher molecular weight carboxylic acids have molecular weights up to about 10,000, more preferably up to about 7500, more preferably up to about 5000. Preferred higher molecular weight carboxylic acids are those containing hydrocarbyl groups of at least about 18 carbon atoms, preferably at least about 30 carbon atoms, more preferably at least about 40 carbon atoms, more preferably at least about 50 carbon atoms.

The higher molecular weight carboxylic acids may also be prepared by halogenating a high molecular weight hydrocarbon such as the above-described olefin polymers to produce a polyhalogenated product, converting the polyhalogenated product to a polynitrile, and then hydrolyzing the polynitrile. They may be prepared by oxidation of a high molecular weight polyhydric alcohol with potassium permanganate, nitric acid, or a similar oxidizing agent. Another method involves the reaction of an olefin or a polar-substituted hydrocarbon such as a chloropolyisobutene with an unsaturated poly-

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carboxylic acid such as 2-pentene-1,3,5-tricarboxylic acid prepared by dehydration of citric acid.

Monocarboxylic acids may be obtained by oxidizing a monoalcohol with potassium permanganate or by reacting a halogenated high molecular weight olefin polymer with a ketene. Another convenient method for preparing monocarboxylic acid involves the reaction of metallic sodium with an acetoacetic ester or a malonic ester of an alkanol to form a sodium derivative of the ester and the subsequent reaction of the sodium derivative with a halogenated high molecular weight hydrocarbon such as brominated wax or brominated polyisobutene.

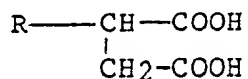
Monocarboxylic and polycarboxylic acids can also be obtained by reacting chlorinated mono- and polycarboxylic acids, anhydrides, acyl halides, and the like with ethylenically unsaturated hydrocarbons or ethylenically unsaturated substituted hydrocarbons such as the polyolefins and substituted polyolefins described hereinbefore in the manner described in U.S. Patent 3,340,281, this patent being incorporated herein by reference.

The monocarboxylic and polycarboxylic acid anhydrides can be obtained by dehydrating the corresponding acids. Dehydration is readily accomplished by heating the acid to a temperature above about 70°C, preferably in the presence of a dehydration agent, e.g., acetic anhydride. Cyclic anhydrides are usually obtained from polycarboxylic acids having acid groups separated by no more than three carbon atoms such as substituted succinic or glutaric acid, whereas linear anhydrides are usually obtained from polycarboxylic acids having the acid groups separated by four or more carbon atoms.

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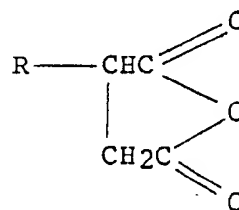
The acid halides of the monocarboxylic and polycarboxylic acids can be prepared by the reaction of the acids or their anhydrides with a halogenating agent such as phosphorus tribromide, phosphorus pentachloride, or thionyl chloride.

Hydrocarbyl-substituted succinic acids and the anhydride, acid halide and ester derivatives thereof can be prepared by reacting maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon such as a chlorinated polyolefin. The reaction involves merely heating the two reactants at a temperature in the range of about 100°C to about 300°C, preferably, about 100°C to about 200°C. The product from this reaction is a hydrocarbyl-substituted succinic anhydride wherein the substituent is derived from the olefin or chlorinated hydrocarbon. The product may be hydrogenated to remove all or a portion of any ethylenically unsaturated covalent linkages by standard hydrogenation procedures, if desired. The hydrocarbyl-substituted succinic anhydrides may be hydrolyzed by treatment with water or steam to the corresponding acid and either the anhydride or the acid may be converted to the corresponding acid halide or ester by reacting with a phosphorus halide, phenol or alcohol. Useful higher molecular weight hydrocarbyl-substituted succinic acids and anhydrides are represented by the formulae



(IIA)

or

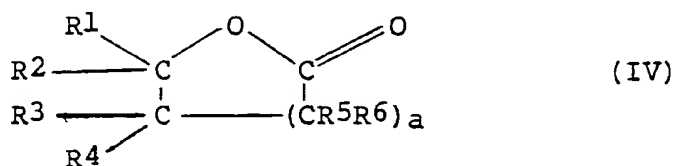


(IIIA)

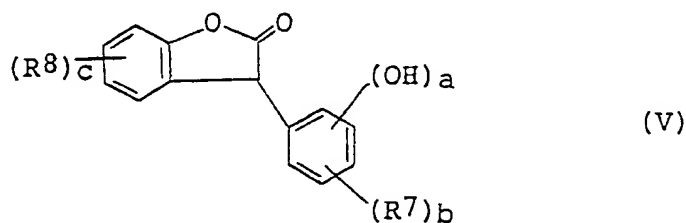
-20-

wherein in Formulae IIA and IIIA, R contains at least about 18 carbon atoms, more preferably at least about 30 carbon atoms, more preferably at least about 40 carbon atoms, more preferably at least about 50 carbon atoms. The number average molecular weight for R will generally not exceed about 100,000, preferably it will not exceed about 10,000, more preferably it will not exceed about 7500, more preferably it will not exceed about 5000.

A group of carboxylic acid derivatives that are particularly useful in making the salts (A) of the invention are the lactones represented by the formula



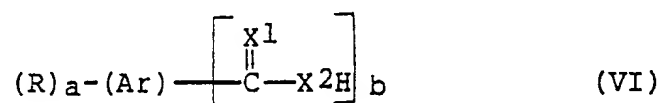
wherein in Formula IV, R1, R2, R3, R4, R5 and R6 are independently H or hydrocarbyl groups of from 1 to about 30 carbon atoms; R2 and R3 can be linked together to form an aliphatic or aromatic ring; and a is a number in the range of zero to about 4. Within this group the lactones represented by the following formula are particularly useful



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wherein in Formula V, R<sup>7</sup> and R<sup>8</sup> are aliphatic hydrocarbyl groups of from 1 to about 30 carbon atoms, a and b are numbers in the range of zero to 5 with the proviso that the sum of a and b does not exceed 5, and c is a number in the range of zero to 4. The procedures for preparing lactones of this type through intramolecular cyclization of hydroxy-containing carboxylic acids accompanied by the elimination of water are well known in the art. Generally, the cyclization is promoted by the presence of materials such as acetic anhydride, and the reaction is effected by heating the mixtures to elevated temperatures such as the reflux temperature while removing volatile materials including water.

A preferred group of carboxylic acids useful in preparing the salts (A) of the present invention are the aromatic carboxylic acids. These acids can be represented by the formula



wherein in Formula VI, R is an aliphatic hydrocarbyl group of preferably about 4 to about 400 carbon atoms, a is a number in the range of zero to about 4, Ar is an aromatic group, X<sup>1</sup> and X<sup>2</sup> are independently sulfur or oxygen, and b is a number in the range of from 1 to about 4, with the proviso that the sum of a and b does not exceed the number of unsatisfied valences of Ar. Preferably, R and a are such that there is an average of at least about 8 aliphatic carbon atoms provided by the R groups in each compound represented by Formula VI.

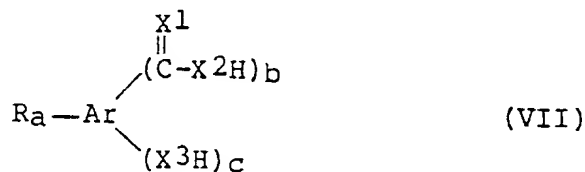
The aromatic group Ar in Formula VI may have the same structure as any of the aromatic groups Ar

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discussed below under the heading "Phenols". Examples of the aromatic groups that are useful herein include the polyvalent aromatic groups derived from benzene, naphthalene, anthracene, phenanthrene, indene, fluorene, biphenyl, and the like. Generally, the Ar groups used herein are polyvalent nuclei derived from benzene or naphthalene such as phenylenes and naphthylene, e.g., methylphenylenes, ethoxyphenylenes, nitrophenylenes, isopropylphenylenes, hydroxyphenylenes, mercaptophenylenes, N,N-diethylaminophenylenes, chlorophenylenes, dipropoxynaphthylenes, triethylnaphthylenes, and similar tri-, tetra-, pentavalent nuclei thereof, etc. These Ar groups may contain non-hydrocarbon substituents, for example, such diverse substituents as lower alkoxy, lower alkyl mercapto, nitro, halo, alkyl or alkenyl groups of less than about 4 carbon atoms, hydroxy, mercapto, and the like.

Examples of the R groups in Formula VI include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, docosyl, tetracontyl, 5-chlorohexyl, 4-ethoxypentyl, 4-hexenyl, 3-cyclohexyloctyl, 4-(p-chlorophenyl)-octyl, 2,3,5-trimethylheptyl, 4-ethyl-5-methyloctyl, and substituents derived from polymerized olefins such as polychloroprenes, polyethylenes, polypropylenes, polyisobutylenes, ethylene-propylene copolymers, chlorinated olefin polymers, oxidized ethylene-propylene copolymers, and the like.

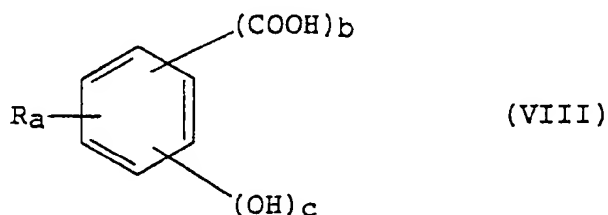
A group of useful carboxylic acids are those of the formula



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wherein in Formula VII, R, Ar, X<sub>1</sub>, X<sub>2</sub>, a and b are as defined in Formula VI, X<sub>3</sub> is oxygen or sulfur, and c is a number in the range of 1 to about 4, usually 1 to about 2, with the proviso that the sum of a, b and c does not exceed the unsatisfied valences of Ar.

Within this group, a useful class of carboxylic acids are those of the formula



wherein in Formula VIII, R is an aliphatic hydrocarbyl group preferably containing from about 4 to about 400 carbon atoms, a is a number in the range of from zero to about 4, preferably 1 to about 3; b is a number in the range of 1 to about 4, preferably 1 to about 2, c is a number in the range of 1 to about 4, preferably 1 to about 2, and more preferably 1; with the proviso that the sum of a, b and c does not exceed 6. Preferably, R and a are such that the acid molecules contain at least an average of about 12 aliphatic carbon atoms in the aliphatic hydrocarbon substituents per acid molecule.

Also useful are the aliphatic hydrocarbon-substituted salicyclic acids wherein each aliphatic hydrocarbon substituent contains an average of at least about 8 carbon atoms per substituent and 1 to 3 substituents per molecule. Salts prepared from such salicyclic acids wherein the aliphatic hydrocarbon substituents are derived from polymerized olefins, particularly polymerized lower 1-mono-olefins such as polyethylene, polypro-

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pylene, polyisobutylene, ethylene/propylene copolymers and the like and having average carbon contents of about 30 to about 400 carbon atoms are particularly useful.

The aromatic carboxylic acids corresponding to Formulae VII and VIII above are well known or can be prepared according to procedures known in the art. Carboxylic acids of the type illustrated by these formulae and processes for preparing their neutral and basic metal salts are well known and disclosed, for example, in U.S. Patents 2,197,832; 2,197,835; 2,252,662; 2,252,664; 2,714,092; 3,410,798; and 3,595,791.

Sulfur-Containing Acids:

The sulfur-containing acids useful in making salts (A) of the invention include the sulfonic, sulfamic, thiosulfonic, sulfinic, sulfenic, partial ester sulfuric, sulfurous and thiosulfuric acids. Generally they are salts of carbocyclic or aliphatic sulfonic acids.

The carbocyclic sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic compounds. The oil-soluble sulfonates can be represented for the most part by the following formulae:



In the above Formulae IX and X, T is a cyclic nucleus such as, for example, benzene, naphthalene, anthracene, phenanthrene, diphenylene oxide, thianthrene, phenothioxine, diphenylene sulfide, phenothiazine, diphenyl oxide, diphenyl sulfide, diphenylamine, cyclohexane, petroleum naphthenes, decahydro-naphthalene, cyclopent-

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tane, etc.; R<sub>1</sub> is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, carboalkoxyalkyl, etc.; a is at least 1, and R<sub>1a</sub>+T contains a total of at least about 15 carbon atoms. R<sub>2</sub> is an aliphatic hydrocarbyl group containing at least about 15 carbon atoms. Examples of R<sub>2</sub> are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R<sub>2</sub> are groups derived from petrolatum, saturated and unsaturated paraffin wax, and polyolefins, including polymerized C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub>, etc., olefins containing from about 15 to 7000 or more carbon atoms. The groups T, R<sub>1</sub>, and R<sub>2</sub> in the above Formulae IX and X can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, disulfide, etc. In Formula IX, a and b are at least 1, and likewise in Formula X, a is at least 1.

The following are specific examples of oil-soluble sulfonic acids within the scope of Formulae IX and X above, and it is to be understood that such examples serve also to illustrate the salts of such sulfonic acids useful in this invention. In other words, for every sulfonic acid enumerated it is intended that the corresponding neutral and basic metal salts thereof are also understood to be illustrated. Such sulfonic acids are mahogany sulfonic acids; bright stock sulfonic acids; sulfonic acids derived from lubricating oil fractions having a Saybolt viscosity from about 100 seconds at 100°F to about 200 seconds at 210°F; petrolatum sulfonic acids; mono- and poly-wax-substituted sulfonic and polysulfonic acids of, e.g., benzene, naphthalene, phenol, diphenyl ether, naphthalene disulfide, diphenylamine, thiophene, alpha-chloronaphthalene, etc.; other

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substituted sulfonic acids such as alkyl benzene sulfonic acids (where the alkyl group has at least 8 carbons), cetylphenol mono-sulfide sulfonic acids, dicetyl thianthrene disulfonic acids, dilauryl beta naphthyl sulfonic acids, dicapryl nitronaphthalene sulfonic acids, and alkaryl sulfonic acids such as dodecyl benzene "bottoms" sulfonic acids.

The latter are acids derived from benzene which has been alkylated with propylene tetramers or isobutene trimers to introduce 1, 2, 3, or more branched-chain C12 substituents on the benzene ring. Dodecyl benzene bottoms, principally mixtures of mono- and di-dodecyl benzenes, are available as by-products from the manufacture of household detergents. Similar products obtained from alkylation bottoms formed during manufacture of linear alkyl sulfonates (LAS) are also useful in making the sulfonates used in this invention.

The production of sulfonates from detergent manufactured by-products by reaction with, e.g., SO<sub>3</sub>, is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

Other descriptions of neutral and basic sulfonate salts and techniques for making them can be found in the following U.S. Patents: 2,174,110; 2,174,506; 2,174,508; 2,193,824; 2,197,800; 2,202,781; 2,212,786; 2,213,360; 2,228,598; 2,233,676; 2,239,974; 2,263,312; 2,276,090; 2,276,097; 2,315,514; 2,319,121; 2,321,022; 2,333,568; 2,333,788; 2,335,359; 2,337,552; 2,346,568; 2,366,027; 2,374,193; 2,383,319; 3,312,618; 3,471,403; 3,488,284; 3,595,790; and 3,798,012. These patents are

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hereby incorporated by reference for their disclosures in this regard.

Also included are aliphatic sulfonic acids such as paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, hexapropylene sulfonic acids, tetra-amylene sulfonic acids, polyisobutene sulfonic acids wherein the polyisobutene contains from 20 to 7000 or more carbon atoms, chloro-substituted paraffin wax sulfonic acids, nitroparaffin wax sulfonic acids, etc.; cycloaliphatic sulfonic acids such as petroleum naphthene sulfonic acids, cetyl cyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, bis-(di-isobutyl) cyclohexyl sulfonic acids, mono- or poly-wax-substituted cyclohexyl sulfonic acids, etc.

With respect to the sulfonic acids or salts thereof described herein and in the appended claims, it is intended herein to employ the term "petroleum sulfonic acids" or "petroleum sulfonates" to cover all sulfonic acids or the salts thereof derived from petroleum products. A useful group of petroleum sulfonic acids are the mahogany sulfonic acids (so called because of their reddish-brown color) obtained as a by-product from the manufacture of petroleum white oils by a sulfuric acid process.

Generally neutral and basic salts of the above-described synthetic and petroleum sulfonic acids are useful in the practice of this invention.

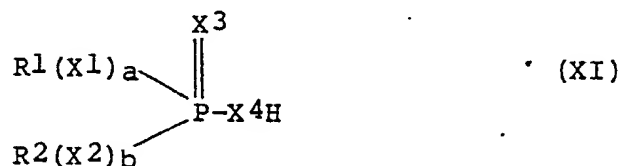
Other patents specifically describing techniques for making basic salts of the hereinabove-described sulfonic acids, carboxylic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,904; 2,616,905; 2,616,906; 2,616,911; 2,616,924;

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2,616,925; 2,617,049; 2,777,874; 3,027,325; 3,256,186; 3,282,835; 3,384,585; 3,373,108; 3,365,396; 3,342,733; 3,320,162; 3,312,618; 3,318,809; 3,471,403; 3,488,284; 3,595,790; and 3,629,109. The disclosures of these patents are hereby incorporated in this present specification for their disclosures in this regard as well as for their disclosure of specific suitable basic metal salts.

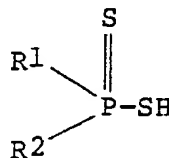
Phosphorus-Containing Acids:

The phosphorus-containing acids useful in making the salts (A) of the invention can be represented by the formula



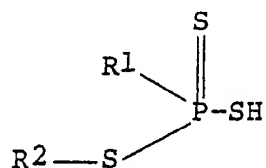
wherein in Formula XI,  $\text{X}^1$ ,  $\text{X}^2$ ,  $\text{X}^3$  and  $\text{X}^4$  are independently oxygen or sulfur;  $a$  and  $b$  are independently zero or one, and  $\text{R}^1$  and  $\text{R}^2$  are independently hydrocarbyl groups. Illustrative examples of some preferred phosphorus-containing acids include:

1. Dihydrocarbyl phosphinodithioic acids corresponding to the formula

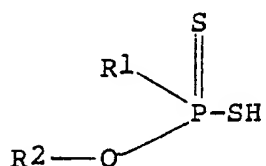


2. S-hydrocarbyl hydrocarbyl phosphonotrithioic acids corresponding to the formula

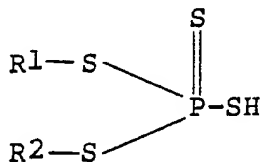
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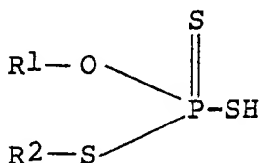
3. O-hydrocarbyl hydrocarbyl phosphonodithioic acids corresponding to the formula



4. S,S-dihydrocarbyl phosphorotetrathioic acids corresponding to the formula

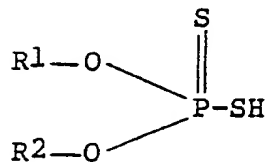


5. O,S-dihydrocarbyl phosphorotrithioic acids corresponding to the formula

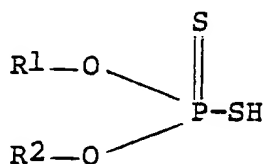


6. O,O-dihydrocarbyl phosphorodithioic acids corresponding to the formula

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Preferred acids of the formula



are readily obtainable by the reaction of phosphorus pentasulfide (P<sub>2</sub>S<sub>5</sub>) and an alcohol or a phenol. The reaction involves mixing at a temperature of about 20°C to about 200°C, four moles of alcohol or a phenol with one mole of phosphorus pentasulfide. Hydrogen sulfide is liberated in this reaction. The oxygen-containing analogs of these acids are conveniently prepared by treating the dithioic acid with water or steam which, in effect, replaces one or both of the sulfur atoms.

Preferred phosphorus-containing acids are phosphorus- and sulfur-containing acids. These preferred acids preferably include those acids wherein at least one X<sub>3</sub> or X<sub>4</sub> is sulfur, and more preferably both X<sub>3</sub> and X<sub>4</sub> are sulfur, at least one X<sub>1</sub> or X<sub>2</sub> is oxygen or sulfur, more preferably both X<sub>1</sub> and X<sub>2</sub> are oxygen, and a and b are each 1. Mixtures of these acids may be employed in accordance with this invention.

R<sub>1</sub> and R<sub>2</sub> are independently hydrocarbyl groups that are preferably free from acetylenic unsaturation and usually also from ethylenic unsaturation and preferably have from about 1 to about 50 carbon atoms,

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more preferably from about 1 to about 30 carbon atoms, and more preferably from about 3 to about 18 carbon atoms, more preferably from about 4 to about 8 carbon atoms. Each R<sub>1</sub> and R<sub>2</sub> can be the same as the other, although they may be different and either or both may be mixtures. Examples of preferred R<sub>1</sub> and R<sub>2</sub> groups include t-butyl, isobutyl, amyl, isooctyl, decyl, dodecyl, eicosyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkyl naphthyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl, alkyl naphthylalkyl, and the like.

Phenols:

The phenols useful in making the salts (A) of the invention can be represented by the formula



wherein in Formula XII, R is a hydrocarbyl group of from about 4 to about 400 carbon atoms; Ar is an aromatic group; a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar. Preferably, a and b are independently numbers in the range of 1 to about 4, more preferably 1 to about 2. R and a are preferably such that there is an average of at least about 8 aliphatic carbon atoms provided by the R groups for each phenol compound represented by Formula XII.

While the term "phenol" is used herein, it is to be understood that this term is not intended to limit the aromatic group of the phenol to benzene. Accordingly, it is to be understood that the aromatic group as represented by "Ar" in Formula XII, as well as elsewhere in other formulae in this specification and in the

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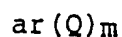
appended claims, can be mononuclear such as a phenyl, a pyridyl, a thienyl, or polynuclear. The polynuclear groups can be of the fused type wherein an aromatic nucleus is fused at two points to another nucleus such as found in naphthyl, anthranyl, azanaphthyl, etc. The polynuclear group can also be of the linked type wherein at least two nuclei (either mononuclear or polynuclear) are linked through bridging linkages to each other. These bridging linkages can be chosen from the group consisting of carbon-to-carbon single bonds, ether linkages, keto linkages, sulfide linkages, polysulfide linkages of 2 to about 6 sulfur atoms, sulfinyl linkages, sulfonyl linkages, alkylene linkages, alkylidene linkages, lower alkylene ether linkages, alkylene keto linkages, lower alkylene sulfur linkages, lower alkylene polysulfide linkages of 2 to about 6 carbon atoms, amino linkages, polyamino linkages and mixtures of such divalent bridging linkages. In certain instances, more than one bridging linkage can be present in Ar between two aromatic nuclei; for example, a fluorene nucleus having two benzene nuclei linked by both a methylene linkage and a covalent bond. Such a nucleus may be considered to have three nuclei but only two of them are aromatic. Normally, however, Ar will contain only carbon atoms in the aromatic nuclei per se (plus any alkyl or alkoxy substituent present).

The number of aromatic nuclei, fused, linked or both, in Ar can play a role in determining the integer values of a and b in Formula XII. For example, when Ar contains a single aromatic nucleus, the sum of a and b is from 2 to 6. When Ar contains two aromatic nuclei, the sum of a and b is from 2 to 10. With a tri-nuclear Ar moiety, the sum of a and b is from 2 to 15. The

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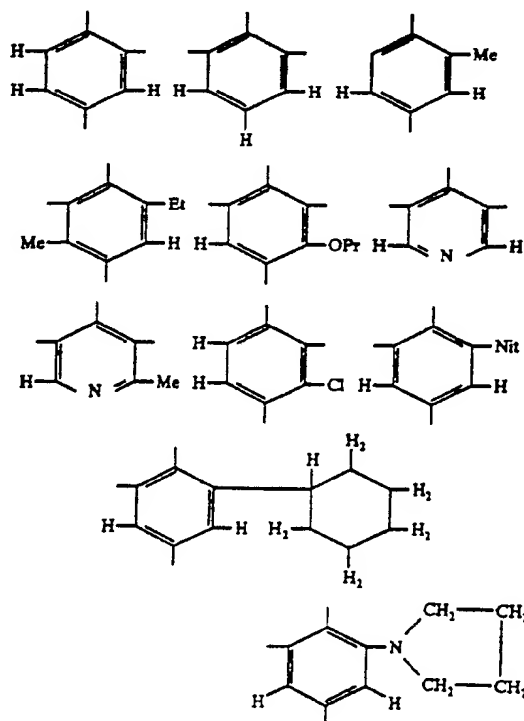
value for the sum of a and b is limited by the fact that it cannot exceed the total number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar.

The single ring aromatic nucleus which can be the Ar group can be represented by the general formula



wherein ar represents a single ring aromatic nucleus (e.g., benzene) of 4 to 10 carbons, each Q independently represents a lower alkyl group, lower alkoxy group, nitro group, or halogen atom, and m is 0 to 4. Halogen atoms include fluorine, chlorine, bromine and iodine atoms; usually, the halogen atoms are fluorine and chlorine atoms.

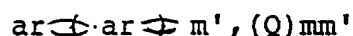
Specific examples of when Ar is a single ring aromatic group include the following:




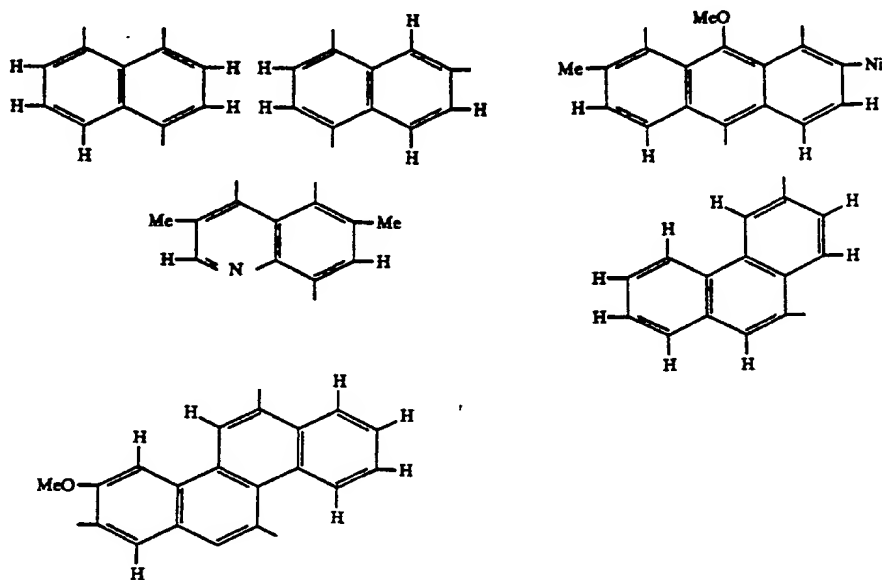
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etc., wherein Me is methyl, Et is ethyl, Pr is propyl, and Nit is nitro.

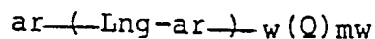
When Ar is a polynuclear fused-ring aromatic group, it can be represented by the general formula



wherein ar, Q and m are as defined hereinabove, m' is 1 to 4 and  represent a pair of fusing bonds fusing two rings so as to make two carbon atoms part of the rings of each of two adjacent rings. Specific examples of when Ar is a fused ring aromatic group include:



When the aromatic group Ar is a linked polynuclear aromatic group it can be represented by the general formula

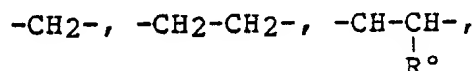


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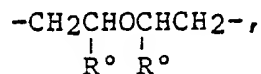
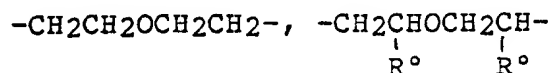
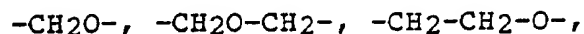
wherein  $w$  is an integer of 1 to about 20,  $ar$  is as described above with the proviso that there are at least two unsatisfied (i.e., free) valences in the total of  $ar$  groups,  $Q$  and  $m$  are as defined hereinbefore, and each  $Lng$  is a bridging linkage individually chosen from the group consisting of carbon-to-carbon single bonds, ether linkages (e.g.,  $-O-$ ), keto linkages (e.g.,



sulfide linkages (e.g.,  $-S-$ ), polysulfide linkages of 2 to 6 sulfur atoms (e.g.,  $-S_2-$  to  $-S_6-$ ), sulfinyl linkages (e.g.,  $-S(O)-$ ), sulfonyl linkages (e.g.,  $-S(O)_2-$ ), lower alkylene linkages (e.g.,



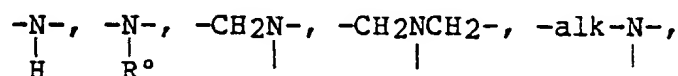
etc.), di(lower alkyl)-methylene linkages (e.g.,  $CR^o_2-$ ), lower alkylene ether linkages (e.g.,



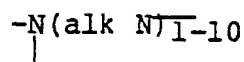
etc.), lower alkylene sulfide linkages (e.g., wherein one or more  $-O-$ 's in the lower alkylene ether linkages is replaced with an  $-S-$  atom), lower alkylene polysulf-

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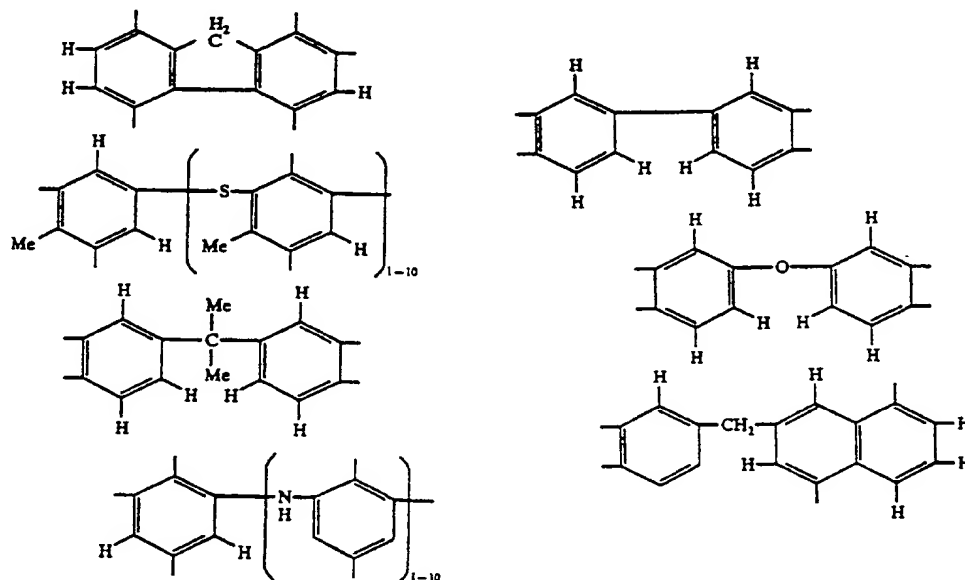
ide linkages (e.g., wherein one or more -O-'s is replaced with a -S-2-6 group), amino linkages (e.g.,



where alk is lower alkylene, etc.), polyamino linkages (e.g.,



where the unsatisfied free N valences are taken up with H atoms or R<sup>o</sup> groups), and mixtures of such bridging linkages (each R<sup>o</sup> being a lower alkyl group). It is also possible that one or more of the ar groups in the above-linked aromatic group can be replaced by fused nuclei such as ar  $\rightleftharpoons$  ar  $\rightleftharpoons$  m'. Specific examples of when Ar is a linked polynuclear aromatic group include:



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Usually all these Ar groups are unsubstituted except for the R and -O- groups (and any bridging groups).

For such reasons as cost, availability, performance, etc., the Ar group is normally a benzene nucleus, lower alkylene bridged benzene nucleus, or a naphthalene nucleus.

The R group in Formula XII is a hydrocarbyl group that is directly bonded to the aromatic group Ar. R preferably contains about 6 to about 80 carbon atoms, preferably about 6 to about 30 carbon atoms, more preferably about 8 to about 25 carbon atoms, and advantageously about 8 to about 15 carbon atoms. Examples of R groups include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, dodecosyl, tetracontyl, 5-chlorohexyl, 4-ethoxypentyl, 4-hexenyl, 3-cyclohexyloctyl, 4-(p-chlorophenyl)-octyl, 2,3,5-trimethylheptyl, 4-ethyl-5-methyloctyl, and substituents derived from polymerized olefins such as polychloroprenes, polyethylenes, polypropylenes, polyisobutylenes, ethylene-propylene copolymers, chlorinated olefin polymers, oxidized ethylene-propylene copolymers, propylene tetramer and tri(isobutene).

The attachment of the hydrocarbyl group R to the aromatic group Ar can be accomplished by a number of techniques well known to those skilled in the art. One particularly suitable technique is the Friedel-Crafts reaction, wherein an olefin (e.g., a polymer containing an olefinic bond), or halogenated or hydrohalogenated analog thereof, is reacted with a phenol. The reaction occurs in the presence of a Lewis acid catalyst (e.g., boron trifluoride and its complexes with ethers, phenols, hydrogen fluoride, aluminum chloride, aluminum bromide, zinc dichloride, etc.). Methods and conditions

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for carrying out such reactions are well known to those skilled in the art. See, for example, the discussion in the article entitled, "Alkylation of Phenols" in "Kirk-Othmer Encyclopedia of Chemical Technology", Second Edition, Vol. 1, pages 894-895, Interscience Publishers, a division of John Wiley and Company, New York, 1963. Other equally appropriate and convenient techniques for attaching the hydrocarbyl group R to the aromatic group Ar will be apparent to those skilled in the art.

As will be appreciated from inspection of Formula XII, the phenol group of the salt (A) of this invention contains at least one R group, as defined above, and OH. Each of the foregoing must be attached to a carbon atom which is a part of an aromatic nucleus in the Ar group. They need not, however, each be attached to the same aromatic ring if more than one aromatic nucleus is present in the Ar group.

Boron-Containing Salts (A):

The boron-containing neutral or basic metal salts (A) of the invention are prepared by the process comprising reacting (1) at least one acidic organic compound or precursor thereof; (2) at least one metal-containing compound selected from the group consisting of alkali metals, alkaline earth metals, zinc, copper, aluminum or a mixture of two or more thereof; (3) at least one boron compound; and (4) at least one promoter.

The acid organic compounds can be any of the above-discussed carboxylic acids or acid-producing compounds, sulfur-containing acids, phosphorus-containing acids or phenols. The acid (1) can also be a mixture of two or more of these.

The metal-containing compound (2) is preferably a metal oxide, metal hydroxide, metal halide, metal

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carbonate or metal borate. It can also be a mixture of two or more of the foregoing. Preferred metals for the metal-containing compounds (2) include lithium, sodium, magnesium, calcium, potassium, barium, aluminum, zinc and copper. Mixtures of two or more of the foregoing metals can be used. Particularly preferred metals are sodium, magnesium, calcium or mixtures of two or more thereof.

The boron compounds (3) include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acids such as boronic acid (i.e., alkyl-B(OH)<sub>2</sub> or aryl-B(OH)<sub>2</sub>), boric acid (i.e., H<sub>3</sub>BO<sub>3</sub>), tetraboric acid (i.e., H<sub>2</sub>B<sub>4</sub>O<sub>7</sub>), metaboric acid (i.e., HBO<sub>2</sub>), boron anhydrides, boron amides and various esters of such boron acids. The use of complexes of boron trihalide with ethers, organic acids, inorganic acids, or hydrocarbons is a convenient means of introducing the boron reactant into the reaction mixture. Such complexes are known and are exemplified by boron-trifluoride-triethyl ester, boron trifluoride-phosphoric acid, boron trichloride-chloroacetic acid, boron tribromide-dioxane, and boron trifluoride-methyl ethyl ether.

Specific examples of boronic acids include methyl boronic acid, phenyl-boronic acid, cyclohexyl boronic acid, p-heptylphenyl boronic acid and dodecyl boronic acid.

The boron acid esters include especially mono-, di-, and tri-organic esters of boric acid with alcohols or phenols such as, e.g., methanol, ethanol, isopropanol, cyclohexanol, cyclopentanol, 1-octanol, 2-octanol, dodecanol, behenyl alcohol, oleyl alcohol, stearyl alcohol, benzyl alcohol, 2-butyl cyclohexanol, ethylene

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glycol, propylene glycol, trimethylene glycol, 1,3-butanediol, 2,4-hexanediol, 1,2-cyclohexanediol, 1,3-octanediol, glycerol, pentaerythritol diethylene glycol, carbitol, Cellosolve, triethylene glycol, tripropylene glycol, phenol, naphthol, p-butylphenol, o,p-diheptylphenol, n-cyclohexylphenol, 2,2-bis-(p-hydroxyphenyl)propane, polyisobutene (molecular weight of 1500)-substituted phenol, ethylene chlorohydrin, o-chlorophenol, m-nitrophenol, 6-bromo-octanol, and 7-keto-decanol. Lower alcohols, 1,2-glycols, and 1-3-glycols, i.e., those having less than about 8 carbon atoms are especially useful for preparing the boric acid esters for the purpose of this invention.

Methods for preparing the esters of boron acid are known and disclosed in the art (such as, "Chemical Reviews," pp. 959-1064, Vol. 56). Thus, one method involves the reaction of boron trichloride with 3 moles of an alcohol or a phenol to result in a tri-organic borate. Another method involves the reaction of boric oxide with an alcohol or a phenol. Another method involves the direct esterification of tetra boric acid with 3 moles of an alcohol or a phenol. Still another method involves the direct esterification of boric acid with a glycol to form, e.g., a cyclic alkylene borate.

The promoter (4) is a chemical employed to facilitate the incorporation of metal into the basic metal compositions. Among the chemicals useful as promoters are water, ammonium hydroxide, organic acids of up to about 8 carbon atoms, nitric acid, sulfuric acid, hydrochloric acid, metal complexing agents such as alkyl salicylaloxime, and alkali metal hydroxides such as lithium hydroxide, sodium hydroxide and potassium hydroxide, and mono- and polyhydric alcohols of up to

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about 30 carbon atoms. Examples of the alcohols include methanol, ethanol, isopropanol, cyclohexanol, dodecanol, decanol, behenyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, monomethylether of ethylene glycol, trimethylene glycol, hexamethylene glycol, glycerol, pentaerythritol, benzyl alcohol, phenylethyl alcohol, sorbitol, nitropropanol, chloroethanol, aminoethanol, cinnamyl alcohol, allyl alcohol, and the like. Especially useful are the monohydric alcohols having up to about 10 carbon atoms and mixtures of methanol with higher monohydric alcohols.

The boron-containing salts (A) are preferably formed by reacting the organic acid (1) with a portion of the metal-containing compound (2) to form a neutral metal salt of an organic acid. Additional metal-containing compound (2) is then added along with the boron compound (3) and promoter (4). The contents are heated to reflux and held at reflux for several hours.

Preferred ratios of components (1), (2), (3) and (4) for the above reaction can be determined by the equation (wherein Eqs. means equivalents):

$$\text{Ratio} = \frac{\text{Moles of Boron}}{\text{Eqs of (2)} - \text{Eqs of (1)} - \text{Eqs of acid in (4)} + \text{Eqs of base in (4)}}$$

This ratio is preferably in the range of about 0.2 to about 3, more preferably about 0.5 to about 2.

For purposes of the above equation, one mole of boron is equal to the number of moles of the boron compound (3) times the number of borons present in that boron compound. Thus, if 3.2 moles of boric acid  $\text{H}_3\text{BO}_3$  are used, then the number of moles of boron is 3.2 times 1 or 3.2. If 2 moles of tetraboric acid  $\text{H}_2\text{B}_4\text{O}_7$  are used, the number of moles of boron is  $2 \times 4$  or 8.

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For the purposes of the above equation, one equivalent of a metal is equal to the molecular weight of that metal divided by the valence of the metal ion. Thus, an equivalent weight of sodium is 23 (i.e., 23 divided by 1 = 23) while an equivalent weight of calcium is 20 (i.e., 40 divided by 2 = 20).

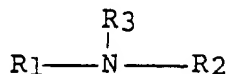
The above reactions may be carried out in the presence of a substantially inert liquid solvent/diluent medium. This solvent/diluent medium desirably serves to maintain contact of the components and facilitates control of the reaction temperature. Examples of suitable solvent/diluent media include aliphatic and aromatic hydrocarbons such as benzene, toluene, naphtha, mineral oil, hexane, chlorinated hydrocarbons such as dichlorobenzene and heptylchloride, and ethers such as methyl n-amylether and n-butylether.

Component (B):

The metal-deactivator (B) preferably comprises at least one benzotriazole which may be substituted or unsubstituted. Examples of suitable compounds are benzotriazole, alkyl-substituted benzotriazole (e.g., tolyltriazole, ethylbenzotriazole, hexylbenzotriazole, octylbenzotriazoles, etc.) aryl-substituted benzotriazole (e.g., phenylbenzotriazoles, etc.), an alkaryl- or arylalk-substituted benzotriazole, and substituted benzotriazoles wherein the substituents may be, for example, hydroxy, alkoxy, halo (especially chloro), nitro, carboxy or carbalkoxy. Preferred are benzotriazole and the alkylbenzotriazoles in which the alkyl group contains 1 to about 20 carbon atoms and especially 1 to about 8 carbon atoms, most desirably benzotriazole and tolyltriazole.

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The metal deactivator (B) can also be the reaction product of at least one of the above benzotriazoles with at least one amine to form a nitrogen-containing composition. The amine can be one or more monoamines or polyamines. These monoamines and polyamines can be primary amines, secondary amines or tertiary amines. The amines can be aliphatic, cycloaliphatic, aromatic, or heterocyclic, including aliphatic-substituted cycloaliphatic, aliphatic-substituted aromatic, aliphatic-substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic-substituted aromatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted aliphatic, aromatic-substituted cycloaliphatic, aromatic-substituted heterocyclic-substituted alicyclic, and heterocyclic-substituted aromatic amines and may be saturated or unsaturated. The amines may also contain non-hydrocarbon substituents or groups as long as these groups do not significantly interfere with the reaction of the amines with the acylating reagents of this invention. Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkyl mercapto, nitro, interrupting groups such as -O- and -S- (e.g., as in such groups as -CH<sub>2</sub>CH<sub>2</sub>-X-CH<sub>2</sub>CH<sub>2</sub>- where X is -O- or -S-). In general, the amine may be characterized by the formula



wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each independently hydrogen or hydrocarbyl, amino-substituted hydrocarbyl, hydroxy-substituted hydrocarbyl, alkoxy-substituted hydrocarbyl, amino, carbamyl, thiocarbamyl, guanlyl and acylimidoyl groups.

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With the exception of the branched polyalkylene polyamine, the polyoxyalkylene polyamines, and the high molecular weight hydrocarbyl-substituted amines described more fully hereafter, the amines ordinarily contain less than about 40 carbon atoms in total and usually not more than about 20 carbon atoms in total.

Aliphatic monoamines include mono-, di- and tri-aliphatic-substituted amines wherein the aliphatic groups can be saturated or unsaturated and straight or branched chain. Such amines include, for example, mono-, di- and tri-alkyl-substituted amines; mono-, di- and tri-alkenyl-substituted amines; and amines having one or more N-alkenyl substituents and one N-alkyl substituents and the like. The total number of carbon atoms in these aliphatic monoamines will, as mentioned before, normally not exceed about 40 and usually not exceed about 20 carbon atoms. Specific examples of such monoamines include ethylamine, diethylamine, triethylamine, n-butylamine, di-n-butylamine, tri-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyllaurylamine, oleylamine, N-methyloctylamine, dodecylamine, octadecylamine, and the like. Examples of cycloaliphatic-substituted aliphatic amines, aromatic-substituted aliphatic amines, and heterocyclic-substituted aliphatic amines, include 2-(cyclohexyl)-ethylamine, benzylamine, phenethylamine, and 3-(furylpropyl)amine.

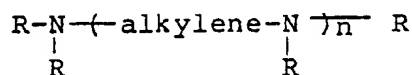
Cycloaliphatic monoamines are those monoamines wherein there is one cycloaliphatic substituent attached directly to the amino nitrogen through a carbon atom in the cyclic ring structure. Examples of cycloaliphatic monoamines include cyclohexylamines, cyclopentylamines, cyclohexenylamines, cyclopentenylamines, N-ethyl-cyclo-

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hexylamine, dicyclohexylamines, and the like. Examples of aliphatic-substituted, aromatic-substituted, and heterocyclic-substituted cycloaliphatic monoamines include propyl-substituted cyclohexylamines, phenyl-substituted cyclopentylamines, and pyran-yl-substituted cyclohexylamine.

Aromatic amines include those monoamines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The aromatic ring will usually be a mononuclear aromatic ring (i.e., one derived from benzene) but can include fused aromatic rings, especially those derived from naphthalene. Examples of aromatic monoamines include aniline, di-(para-methylphenyl)amine, naphthylamine, N-(n-butyl)-aniline, and the like. Examples of aliphatic-substituted, cycloaliphatic-substituted, and heterocyclic-substituted aromatic monoamines are para-ethoxyaniline, para-dodecylaniline, cyclohexyl-substituted naphthylamine, and thienyl-substituted aniline.

The polyamines include principally alkylene amines conforming for the most part to the formula



wherein n is a number preferably less than about 10, each R is independently a hydrogen group or a hydrocarbyl group preferably having up to about 30 carbon atoms, and the alkylene group is preferably a lower alkylene group having less than about 8 carbon atoms. The alkylene amines include principally methylene amines, ethylene amines, butylene amines, propylene amines, pentylene amines, hexylene amines, heptylene

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amines, octylene amines, other polymethylene amines. They are exemplified specifically by: ethylene diamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene) triamine. Higher homologues such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful.

The ethylene amines are especially useful. They are described in some detail under the heading "Ethylene Amines" in Encyclopedia of Chemical Technology, Kirk and Othmer, Vol. 5, pp. 898-905, Interscience Publishers, New York (1950). Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia. The reaction results in the production of somewhat complex mixtures of alkylene amines, including cyclic condensation products such as piperazines. These mixtures find use in the process of this invention. On the other hand, quite satisfactory products may be obtained also by the use of pure alkylene amines. An especially useful alkylene amine for reasons of economy as well as effectiveness of the products derived therefrom is a mixture of ethylene amines prepared by the reaction of ethylene chloride and ammonia and having a composition which corresponds to that of tetraethylene pentamine.

Hydroxyalkyl-substituted alkylene amines, i.e., alkylene amines having one or more hydroxyalkyl substituents on the nitrogen atoms, likewise are contemplated for use herein. Higher homologues such as are obtained by condensation of the above illustrated alkylene amines or hydroxy alkyl-substituted alkylene amines through

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amino radicals or through hydroxy radicals are likewise useful. It will be appreciated that condensation through amino radicals results in a higher amine accompanied with removal of ammonia and that condensation through the hydroxy radicals results in products containing ether linkages accompanied with removal of water.

The metal deactivator (B) can also be the reaction product of at least one of the above benzotriazoles with at least one nitrogen-containing ashless dispersant of the type described below under the heading "Lubricants and Functional Fluids". Particularly preferred are the nitrogen-containing carboxylic dispersants, amine dispersants and Mannich dispersants described below.

The benzotriazole-amine and benzotriazole-ashless dispersant reaction products may be prepared by merely blending the reagents and allowing the reaction to proceed. The reaction may be effected in a substantially inert, normally liquid organic diluent (which may be the oil or diluent constituent of the lubricant or concentrate containing the composition of this invention) such as mineral oil, benzene, toluene, xylene, petroleum naphtha, an aliphatic ether or the like, whereupon it may take place at a temperature as low as about 15°C. Ordinarily, it is preferred to carry out the reaction at temperatures of up to about 160°C, with temperatures in the range of about 60°C to about 140°C being useful.

The proportions of the benzotriazole and amine or ashless dispersant used for the preparation of the reaction products useful as component (B) may vary widely. In general, it is preferred to incorporate as much of the benzotriazole as possible in an oil-dispers-

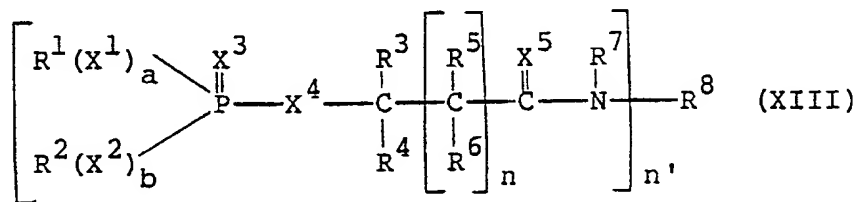
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ible medium and this can be done by using about one equivalent of amine or ashless dispersant per equivalent of benzotriazole. (The equivalent weight of the amine or ashless dispersant is its molecular weight divided by the number of basic nitrogen atoms therein, and that of the benzotriazole is its molecular weight divided by the number of triazole rings therein.) In some instances, however, it may be desirable to use more or less than one equivalent of amine or ashless dispersant per equivalent of benzotriazole.

The precise molecular structures of the benzotriazole-amine and benzotriazole-ashless dispersant reaction products are not known with certainty and are not critical. It is believed, however, that the benzotriazoles are generally more acidic than the amines or ashless dispersants and thus the compositions may comprise amine salts of the benzotriazoles.

Phosphorus-Containing Amides (C-1):

The phosphorus-containing amides (C-1) preferably comprise at least one compound represented by the formula:



wherein in Formula XIII:

x1, x2, x3, x4 and x5 are independent-ly oxygen or sulfur;

R1 and R2 are independently hydrocarbyl groups;

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R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> are independently hydrogen, halogen or hydrocarbyl groups;

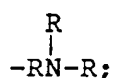
a and b are independently zero or 1;

n is zero or 1;

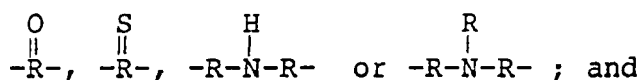
n' is 1, 2 or 3;

with the proviso that:

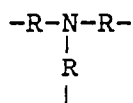
(1) when n' is 1, R<sub>8</sub> is hydrogen, -R, -ROH, -ROR, -RSR or



(2) when n' is 2, R<sub>8</sub> is a coupling group selected from -R-, -R\*- , -R-O-R-, -R-S-R-,



(3) when n' is 3, R<sub>8</sub> is the coupling group



wherein each R is independently a hydrocarbyl group of 1 to about 12 carbon atoms; and R\* is a hydrocarbyl or carboxyhydrocarbyl group of 1 to about 60 carbon atoms.

X<sub>1</sub>, X<sub>2</sub> and X<sub>5</sub> are preferably oxygen. X<sub>3</sub> and X<sub>4</sub> are preferably sulfur.

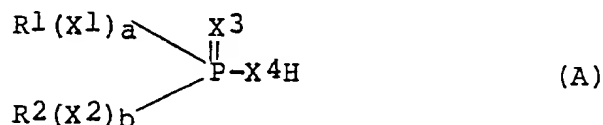
R<sub>1</sub> and R<sub>2</sub> are independently hydrocarbyl groups of from 1 to about 50 carbon atoms, more preferably from 1 to about 30 carbon atoms, more preferably from about 3 to about 18 carbon atoms, more preferably from about 4 to about 8 carbon atoms. Examples of R<sub>1</sub> and R<sub>2</sub> are independently t-butyl, isobutyl, amyl, iso-octyl, decyl, dodecyl, eicosyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylnaphtyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl, alkylnaphtylalkyl groups, and the like.

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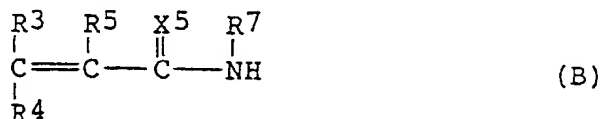
R3, R4, R5, R6 and R7 are independently hydrogen or hydrocarbyl groups of 1 to about 50 carbon atoms, more preferably 1 to about 30 carbon atoms, more preferably 1 to about 18 carbon atoms, more preferably 1 to about 8 carbon atoms. Advantageously, R3, R4, R5, R6 and R7 are independently hydrogen; alkyl groups of from 1 to about 22 carbon atoms; cycloalkyl groups of from about 4 to about 22 carbon atoms; or aromatic, alkyl-substituted aromatic or aromatic-substituted alkyl groups of from about 4 to about 34 carbon atoms.

When R is a linking group, it is preferably methylene. R\* is preferably an alkylene or alkylidene group of 1 to about 28 carbon atoms.

The phosphorus-containing amides represented by Formula XIII can be made by various alternative routes. In one embodiment, the preparation of these amides involves the reaction of a phosphorus-containing acid reactant having the formula



with an acrylamide-type reactant having the formula



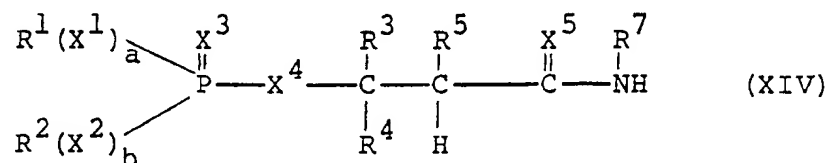
wherein the various R and X groups are as set forth above in Formula XIII. The reactant (A) is described above under the heading "Phosphorus-Containing Acids".

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Examples of reactant (B) include acrylamide, methacrylamide wherein R<sup>5</sup> is methyl, and crotonamide.

The reaction between the reactants (A) and (B) is exothermic and hence only slight heat need be applied thereto. The reaction conveniently can be carried out in an inert atmosphere such as nitrogen at from about 25°C to about 100°C, with from about 70°C to about 90°C being preferred. The reaction can be carried out in the presence or absence of a solvent. Preferably, the reaction takes place in a solvent medium which typically is a hydrocarbon such as toluene, xylene, hexane, heptane, kerosene, fuel oil, an oil of a lubricating viscosity, and the like or a chlorohydrocarbon such as chloroform, carbon tetrachloride, and the like, or an alcohol such as methanol, ethanol, propanol, butanol, 2-ethylhexanol, and the like. The solvent, in addition to acting as such, preferably imparts favorable processing characteristics such as controlling the exothermic reaction as well as preventing unwanted side reactions. The reaction time, while dependent upon temperature, is usually as short as one or two hours or less.

The reaction between the reactants (A) and (B) yields a compound having the formula

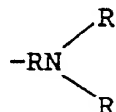


At this point the R<sup>8</sup> group of Formula XIII is hydrogen and n is 1. This reaction product XIV is an intermediate. However, it can also serve as an end product for use as the additive (C-1) of the invention.

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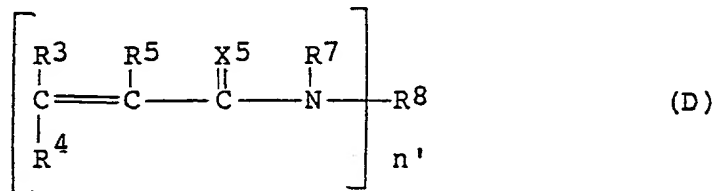
This product is useful in providing lubricants and functional fluids with enhanced load-carrying, extreme pressure, anti-wear and/or corrosion-inhibiting properties.

The intermediate reaction product XIV can be coupled in a manner such as described below and/or further reacted in various ways known to those skilled in the art to include other functional groups R<sup>8</sup> on the nitrogen atom which groups include -ROH, -ROR, -RSR,



wherein R is as defined above with respect to Formula XIII.

In another embodiment of the invention, the preparation of the phosphorus-containing amides XIII involves reacting reactant (A) with a compound having the formula



wherein the various R and X groups and n' are as set forth in Formula XIII.

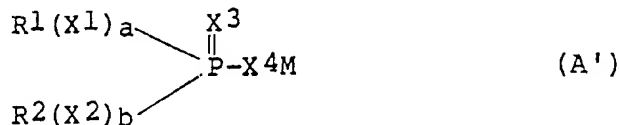
Reactant (D) is similar to reactant (B) except that it is coupled by an R<sup>8</sup> coupling group (i.e., one of the above-indicated groups for R<sup>8</sup> when n'=2 or 3). Accordingly, the definition of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>7</sup> is the same as set forth hereinabove with respect to

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reactant (B). R<sup>8</sup> is the same as discussed above with respect to Formula XIII, when n'=2 or 3, with n' preferably being 2 and R<sup>8</sup> preferably being -CH<sub>2</sub>-O-CH<sub>2</sub>-.

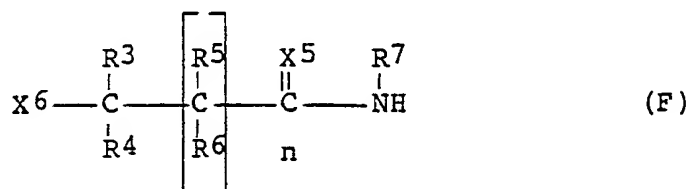
The reaction between the reactants (A) and (D) is exothermic and thus requires only a slight amount of heat. It is preferably carried out in an inert atmosphere at a temperature from about 25°C to about 100°C with from about 70°C to about 90°C being preferred. The reaction time is generally short, for example, on the order of less than an hour or two. Hydrocarbon solvents such as toluene, xylene, hexane, heptane, kerosene, fuel oil, an oil of a lubricating viscosity, and the like or chlorinated hydrocarbon such as chloroform, carbon tetrachloride, and the like, or an alcohol such as methanol, ethanol, propanol, butanol, 2-ethylhexanol, and the like, can be used. Once the product has been formed, the various solvents can be removed by stripping under a vacuum and the like.

Another alternative method of preparing the phosphorus-containing amides of Formula XIII and especially the coupled compounds set forth hereinabove containing an R<sup>6</sup> group is via a displacement reaction. In this reaction, a metal salt of the reactant (A) is used. That is a metal salt according to the following formula

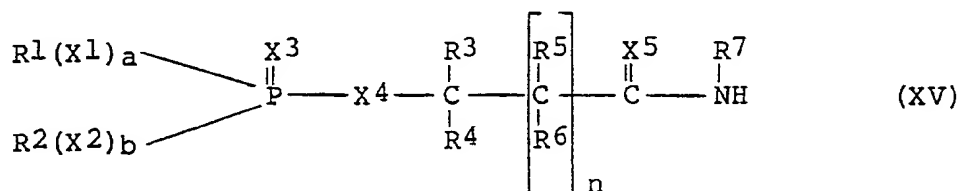


is reacted with a compound of the formula

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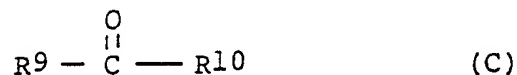
wherein  $\text{X}^1$ ,  $\text{X}^2$ ,  $\text{X}^3$ ,  $\text{X}^4$ ,  $\text{X}^5$ ,  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and  $n$  are the same as set forth above with respect to Formula XIII.  $\text{M}$  is an alkali metal (e.g., sodium, potassium and the like) or an alkaline-earth metal (e.g., manganese, calcium and the like) or hydrogen, with sodium and potassium being preferred.  $\text{X}^6$  is a displaceable halogen or carbon group such as  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ , tosyl, mesyl, and the like. The reaction between reactants  $\text{A}'$  and  $\text{F}$  proceeds in a manner very similar to that set forth above with regard to the reaction product between reactants (A) and (B). Briefly, the reaction is carried out at a temperature of about  $10^\circ\text{C}$  to about  $200^\circ\text{C}$  with from about  $50^\circ\text{C}$  to about  $150^\circ\text{C}$  being preferred. An inert atmosphere such as nitrogen is used. Although not required, the reaction can take place in a menstruum. The solvent also renders by-product salts (e.g.,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{KBr}$ , etc.) insoluble in the reaction medium and which can be removed by filtration. The amounts of reactants  $\text{A}'$  and  $\text{F}$  are generally equivalent amounts. The resulting product has the formula



The reaction product formed by the reaction between reactants (A) and (B) can be coupled by reacting it with a coupling agent (C) which is an aldehyde or

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ketone (or a reaction synthon equivalent of an aldehyde or ketone) of the formula



wherein R9 and R10 are independently hydrogen, alkyl groups of 1 to about 12 carbon atoms, phenyl, or alkyl-substituted phenyl having from about 7 to about 12 carbon atoms. Preferably, coupling agent (C) is an aldehyde (i.e., R10 is H) having a total of 1 to about 3 carbon atoms therein with one carbon atom being preferred. Formaldehyde and paraformaldehyde are preferred; these can result in methylene and dimethylene ether coupling groups.

The coupling reaction preferably takes place in the presence of a strong mineral or organic acid catalyst such as HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>4</sub>PO<sub>4</sub>, CH<sub>3</sub>SO<sub>3</sub>H, p-toluenesulfonic acid, and the like. The amount of the acid catalyst is generally from about 0.3 to about 1.5% by weight, preferably from about 0.8 to about 1.2%, and more preferably from about 0.9 to about 1.1% by weight based upon the weight of the total product formed. Although lesser amounts of catalyst can be utilized, the reaction is generally slower and a smaller fraction of the desired product is formed. The reaction with coupling agent (C) preferably takes place at an initial temperature of from about 80°C to about 120°C, more preferably from about 80°C to about 100°C in an inert atmosphere. The final reaction temperature is generally higher as from about 100°C to about 150°C and preferably from about 125°C to about 135°C.

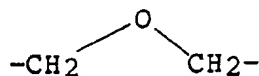
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If it is desired to stop the reaction at the carbinol stage, (Formula XV where X<sup>5</sup> is oxygen) the reaction between (A) and (B) is preferably carried out using basic catalysts (i.e., NaHCO<sub>3</sub>, KHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, KCO<sub>3</sub>, NaOH, KOH, etc.). This reaction mixture can be neutralized with acid and heated to remove water; reacted with H<sub>2</sub>S, NaHS or Na<sub>2</sub>S or other source of S=; or, NH<sub>3</sub> or R"NH<sub>2</sub> where R" is alternatively H, alkyl of 1 to about 60 carbon atoms, aryl, alkyl-substituted, aryl or aryl-substituted alkyl of about 6 to about 30 carbon atoms or acyl of 1 to about 22 carbon atoms.

The ratio of reactant (A) and to reactant (B) that is employed is preferably a 1:1 equivalent weight ratio although greater or lesser amounts can be utilized. A 1:1 equivalent weight ratio of the two reactants is preferable in that otherwise a higher acid number is obtained than desired or one of the reactants is wasted. The amount of reaction product formed and reacted with coupling agent (C) is from about 0.3 to about 3 weight equivalents of reaction product per weight equivalent of said coupling agent (C) with a 1:1 equivalent ratio being preferred. The coupling agent (C) may be a mixture of different couplers and preferably includes paraformaldehyde.

The combination of formaldehyde and phosphorus containing amide compound as described above may couple two amides or may result in the formation of a -CH<sub>2</sub>OH on the nitrogen atom of the amide. Two of such amides with a -CH<sub>2</sub>OH group thereon may then be reacted to form a coupled amide with the coupling group being

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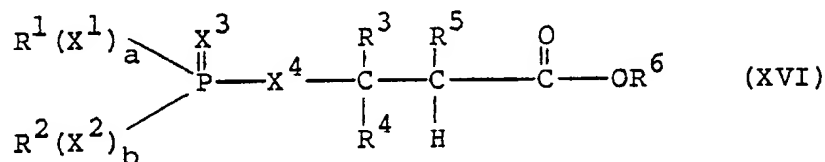


Such a coupling reaction may take place during use of such uncoupled compounds which reaction is endothermic. The endothermic reaction may be beneficial to the load-carrying lubricating properties of the overall oil composition.

Other couplers ( $R^8$  in Formula XIII when  $n'$  is 2 or 3) and functional groups ( $R^8$  in Formula XIII when  $n'$  is 1) can be attached to the nitrogen atoms of the phosphorus-containing amides described above by procedures known to those skilled in the art.

Phosphorus-Containing Esters (C-2):

The phosphorus-containing esters (C-2) of the present invention may be characterized by the structural formula



wherein in Formula XVI,  $x_1$ ,  $x_2$ ,  $x_3$  and  $x_4$  are independently oxygen or sulfur;  $R_1$  and  $R_2$  are independently hydrocarbyl groups;  $R_3$ ,  $R_4$  and  $R_5$  are independently hydrogen or hydrocarbyl groups;  $R_6$  is a hydrocarbyl group; and  $a$  and  $b$  are independently zero or 1.

In Formula XVI,  $x_1$  and  $x_2$  are preferably oxygen, and  $x_3$  and  $x_4$  are preferably sulfur.

$R_1$  and  $R_2$  are independently hydrocarbyl groups of from 1 to about 50 carbon atoms, more prefer-

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ably from 1 to about 30 carbon atoms, more preferably from 3 to about 18 carbon atoms, more preferably from 4 to about 8 carbon atoms. Examples of R<sup>1</sup> and R<sup>2</sup> include independently t-butyl, isobutyl, amyl, isooctyl, decyl, dodecyl, eicosyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylnaphthyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl, alkylnaphthylalkyl groups, and the like.

Preferably, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are independently hydrogen or hydrocarbyl groups of from 1 to about 50 carbon atoms. More preferably, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are independently hydrogen; alkyl groups of from 1 to about 22 carbon atoms; cycloalkyl groups of from about 4 to about 22 carbon atoms; or aromatic, alkyl-substituted aromatic or aromatic-substituted alkyl groups of from about 4 to about 34 carbon atoms.

R<sup>6</sup> is preferably an alkyl group of from 1 to about 22 carbon atoms; a cycloalkyl group of from about 4 to about 22 carbon atoms; or an aromatic, alkyl-substituted aromatic or aromatic-substituted alkyl group of from about 4 to about 34 carbon atoms.

In a particularly preferred embodiment, R<sup>1</sup> and R<sup>2</sup> are independently alkyl groups of from about 3 to about 18 carbon atoms; X<sup>1</sup> and X<sup>2</sup> are oxygen; X<sup>3</sup> and X<sup>4</sup> are sulfur; R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> independently are hydrogen or methyl; and n" is 1.

The phosphorus-containing esters represented by Formula XVI can be prepared by the reaction of the phosphorus-containing acid.



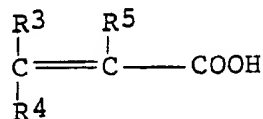
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with a compound represented by the formula



wherein the various R and X groups are as defined with respect to Formula XVI.

Reactant (A) is described above under the heading "Phosphorus-Containing Acids". Reactant (B) may be prepared by the reaction of an alcohol represented by the formula  $\text{R}^6\text{OH}$  with an alpha, beta-unsaturated carboxylic acid represented by the formula



wherein  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are as defined above with respect to Formula XVI.

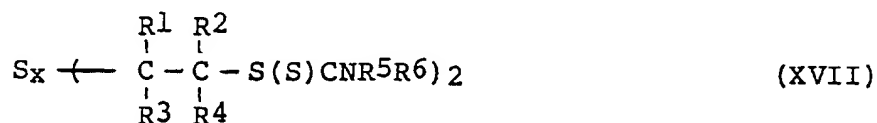
The reaction between reactants (A) and (B) can be carried out by adding over a period of time either reactant (A) or (B) to the other with stirring preferably in the presence of an inert organic solvent, such as benzene, toluene or methylene chloride. The addition is preferably carried out at an elevated temperature, for instance at reflux. The reaction mixture is then refluxed over a further period of time, for instance from 1 to 4 hours. The product is then cooled and neutralized, for instance by washing with aqueous sodium carbonate and then, if desired, with brine. The solvent is then removed by evaporation and then, if desired, the product is steam-distilled. The product may afterwards

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be purified by conventional techniques, for instance by filtering.

Sulfur-Coupled Dithiocarbamates (C-3):

The sulfur-coupled dithiocarbamates (C-3) of the present invention may be characterized by the structural formula



wherein in Formula XVII,  $R^1$ ,  $R^2$  and  $R^3$  are independently H or a hydrocarbyl group;  $R^4$  is H, OH or a hydrocarbyl group;  $R^5$  and  $R^6$  are independently H, a hydrocarbyl group or hydroxyhydrocarbyl group; or  $R^3$  and  $R^4$  together and/or  $R^5$  and  $R^6$  together and/or  $R^1$  and  $R^3$  together and/or  $R^2$  and  $R^4$  together may form cyclic groups, and  $x$  is a number from 1 to about 8.

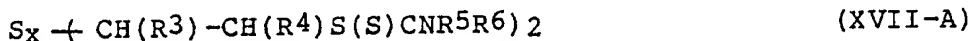
The hydrocarbyl groups of  $R^1$  through  $R^4$  may be straight-chain or branched-chain hydrocarbyl groups. Each of  $R^1$  through  $R^6$  may independently contain from 1 to about 100 carbon atoms, preferably from 1 to about 30 carbon atoms.

The groups  $R^1$  through  $R^4$  may be aliphatic or aromatic groups such as alkyl, cycloalkyl, alkaryl, aralkyl or aryl groups.  $R^3$  and  $R^4$  together and/or  $R^5$  and  $R^6$  together may be alkylene groups containing from about 4 to about 7 carbon atoms. In these embodiments,  $R^3$  and  $R^4$  together with the carbon atom bonded to  $R^3$  and  $R^4$  in Formula XVII will form a cycloalkyl group, and  $R^5$  and  $R^6$ , together with the nitrogen atom bonded to  $R^5$  and  $R^6$  in Formula XVII forms a heterocyclic group.

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Specific examples of hydrocarbyl groups R<sub>1</sub> through R<sub>6</sub> include methyl, ethyl, isopropyl, isobutyl, secondary butyl, cyclohexyl, cyclopentyl, octyl, dodecyl, octadecyl, eicosyl, behenyl, triacontonyl, phenyl, naphthyl, phenethyl, octylphenyl, tolyl, xylyl, dioctadecylphenyl, triethylphenyl, chlorophenyl, methoxyphenyl, dibromophenyl, nitrophenyl, 3-chlorohexyl, etc.

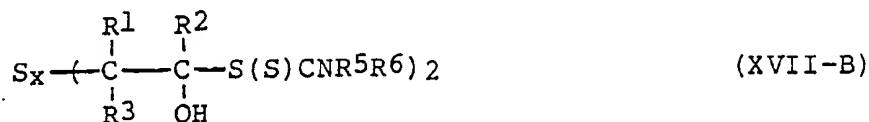
In one embodiment of the present invention, the sulfur-coupled dithiocarbamate is characterized by the structural formula



wherein in Formula XVII-A, x is a number of from 1 to 2, R<sub>3</sub> and R<sub>4</sub> are hydrogen or a hydrocarbyl group, and R<sub>5</sub> and/or R<sub>6</sub> are each individually hydrocarbyl groups.

The hydrocarbyl groups in Formula XVII-A may be any of the hydrocarbyl groups described above with respect to Formula XVII. Generally, R<sub>5</sub> and R<sub>6</sub> will contain from 1 to about 50 carbon atoms, and R<sub>3</sub> and R<sub>4</sub> are hydrocarbyl groups containing from 1 to about 100 carbon atoms.

In another embodiment of the present invention, the dithiocarbamates are characterized by the structural formula



wherein in Formula XVII-B, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>6</sub> and x are as defined above with respect to Formula XVII.

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In one embodiment the sulfur-coupled dithiocarbamates are prepared by a process comprising the steps of

(A) reacting a sulfur halide with about a stoichiometric equivalent of (i) at least one olefinic hydrocarbon or (ii) an aldehyde or ketone at a temperature and for a period of time sufficient to produce a di(halohydrocarbyl)sulfur intermediate or a dialdehyde or diketo sulfur intermediate, and

(B) reacting the intermediate with a salt of a dithiocarbamate in an amount sufficient generally to replace both halo groups with the dithiocarbamate groups or to react with both carbonyl groups of the dialdehyde or diketone.

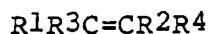
When the starting material is (i) at least one olefinic hydrocarbon, the resulting product is characterized by either Formula XVII or Formula XVII-A or the product is a mixture comprising principally materials characterized by Formulae XVII and XVII-A. When the starting material is (ii) an aldehyde or a ketone, the product is characterized primarily by Formula XVII-B.

The sulfur halide utilized in the first step (A) may be sulfur monochloride (i.e.,  $S_2Cl_2$ ), sulfur dichloride, sulfur monobromide, sulfur dibromide, or mixtures of any of the above sulfur halides with elemental sulfur in varying amounts.

Various olefins and olefin mixtures may be used as the starting material in step (A). Olefin mixtures resulting from the oligomerization of ethylene and/or propylene are available at low cost. The olefinic hydrocarbons contain at least one olefinic double bond which is defined as a non-aromatic double bond. That is, the double bond connects two aliphatic carbon atoms.

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In its broadest sense, the olefin may be defined by the formula



wherein each of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is hydrogen or a hydrocarbyl group as defined above with respect to Formulae XVII, XVII-A or XVII-B. Although diolefinic hydrocarbons may be utilized, it is preferred that the olefin be a monoolefin and the olefin may be a terminal monoolefinic hydrocarbon; that is, those olefins in which  $R_1$  and  $R_3$  are hydrogen and  $R_2$  and/or  $R_4$  are alkyl or aryl. Internal olefinic compounds, e.g., where  $R_1$  and  $R_2$  are alkyl or aryl groups also are useful. Olefinic compounds containing 3 to about 100 carbon atoms and more generally from 3 to about 30 carbon atoms are particularly desirable.

Isobutene, propylene, and their dimers, trimers, tetramers, etc. and mixtures thereof are also useful olefinic compounds. Of these compounds, isobutylene, diisobutylene, triisobutylene and tetraisobutylene are particularly desirable because of their availability.

The product which is obtained from the reaction of a sulfur halide with one or more of the above-identified olefinic hydrocarbons is a di(halohydrocarbyl)sulfide intermediate produced by the addition of the elements of the sulfur halide to the unsaturated carbon atoms of the olefin. The reaction proceeds on mixing of the olefin and the sulfur halide although the rate of the reaction is increased by elevating the temperature of the mixture. Thus, the mixture generally is between  $-20^{\circ}\text{C}$  and  $120^{\circ}\text{C}$  until the reaction is completed. The

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reaction temperature is dictated by the reactivity of the starting olefin and the thermal stability of the reaction product.

Alternatively, the olefin can be warmed to the desired temperature whereupon the sulfur halide can be added dropwise, generally in an inert atmosphere at a rate sufficient to maintain the desired temperature. Following the completion of the addition of the sulfur halide, the reaction mixture may be heated for an extended period to complete the reaction.

The amount of sulfur halide reacted with the olefinic hydrocarbon generally is a stoichiometric equivalent. For example, when a sulfur monohalide is utilized as the sulfur halide source, one mole of sulfur monohalide is reacted with two moles of the olefin or olefin mixture.

Catalysts or reaction promoters may be utilized although they are generally found to be unnecessary. Examples of such catalysts or promoters include the lower aliphatic amines and aromatic amines, especially tertiary amines.

The aldehydes or ketones which may be utilized as a starting material for reaction with a sulfur halide may be characterized by the following formula



wherein  $R^1$ ,  $R^2$  and  $R^3$  are each individually hydrogen or hydrocarbyl groups as defined above with respect to Formulae XVII, XVII-A or XVII-B. When the starting material is an aldehyde, the intermediate will contain two aldehyde carbonyl groups, and when the starting material is a ketone, the sulfur intermediate will contain two keto groups.

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The aldehydes and ketones may be reacted with sulfur halides such as sulfur monochloride, sulfur dichloride, sulfur monobromide, sulfur dibromide, and mixtures of sulfur halide with elemental sulfur.

The reaction of an aldehyde or ketone with a sulfur halide may be effected simply by mixing the two reactants at the desired temperature which may range from about  $-30^{\circ}\text{C}$  to about  $250^{\circ}\text{C}$  or higher. A preferred reaction temperature generally is within the range of from about  $10$  to about  $80^{\circ}\text{C}$ . The reaction may be carried out in the presence of a diluent or solvent such as benzene, naphtha, hexane, carbon tetrachloride, chloroform, mineral oil, etc. The diluent/solvent facilitates the control of the reaction temperature and a thorough mixing of the the reactants.

The relative amounts of the aldehyde or ketone and the sulfur halide may vary over wide ranges. In most instances, the reaction involves two moles of the aldehyde or ketone and one mole of the sulfur halide. In other instances, an excess of either one of the reactants may be used. When sulfur compounds are desired which contain more than two sulfur atoms, (e.g.,  $x$  is an integer from 3-8) these compounds can be obtained by reacting the aldehydes and ketones with a mixture of sulfur halide and sulfur. This is usually accomplished by reacting the sulfur halide and sulfur prior to reaction with the aldehyde or ketone.

Specific examples of aldehydes that can be reacted with sulfur halides include, for example, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, 2-ethyl-1-hexaldehyde, cyclohexanecarboxaldehyde, ( $\text{C}_6\text{H}_{11}\text{CHO}$ ). Examples of ketones include dimethylketone, methylethylketone, diethylketone, methylisopropylketone, methylisobutylketone, etc.

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The sulfur-coupled dithiocarbamates of the present invention are prepared by reacting the above-described sulfur intermediates with a salt of a dithiocarbamate in an amount sufficient to replace the halo groups with dithiocarbamate groups or to react with both carbonyl groups of the dialdehyde or diketone intermediate. The dithiocarbamate salts may be represented by the formula



wherein  $R^5$  and  $R^6$  are each individually hydrogen, hydrocarbyl or hydroxyhydrocarbyl groups and  $X$  is an alkali metal, tertiary amine, or other basic material. The salts of the dithiocarbamic acids may be prepared by the reaction of an amine  $R^5R^6NH$  with carbon disulfide in the presence of a base, usually an alkali metal hydroxide, generally, at a molar ratio of 1:1:1. Preferably the base is an alkali metal hydroxide such as sodium or potassium hydroxide, and more generally, sodium hydroxide. However, the base can be a tertiary amine or in excess of the amine being used on the reaction.

The hydrocarbyl or hydroxyhydrocarbyl groups  $R^5$  and  $R^6$  may contain from 1 to about 50 carbon atoms. Preferably,  $R^5$  and  $R^6$  are lower hydrocarbyl groups. In one embodiment,  $R^5$  and  $R^6$  are alkylene groups containing from about 4 to about 7 carbon atoms, and in this embodiment,  $R^5$  and  $R^6$  together with the nitrogen atom bonded to  $R^5$  and  $R^6$  will form a heterocyclic group. The heterocyclic group (and the alkylene group) may contain other atoms such as oxygen and sulfur.

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Specific examples of the amines ( $R^5R^6NH$ ) used to form the dithiocarbamates include, for example, methylamine, propylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, methylethylamine, methylcyclohexylamine, piperidine, morpholine, dihexylamine, dioctylamine, dicocoamine, methylhydroxyethylamine, di-hydroxyethylamine, piperazine, etc.

The metal salts of dithiocarbamates are known in the art and can be prepared readily by one skilled in the art. One method of preparing alkali metal salts of dithiocarbamic acids involves the reaction of an amine, carbon disulfide and an alkali metal hydroxide. Generally, these reactants are mixed and reacted at low temperatures such as between about zero and  $15^{\circ}C$ . In one embodiment, an aqueous amine is cooled to zero to  $15^{\circ}C$  and carbon disulfide is added dropwise, generally in an inert atmosphere before or during the addition of the alkali metal hydroxide. In another embodiment, the aqueous amine is cooled whereupon the alkali metal hydroxide is added followed by the carbon disulfide. When all of the reactants have been mixed at the low temperature of zero to  $15^{\circ}C$ , the mixture is allowed to warm to ambient temperature with stirring.

The salts of dithiocarbamic acids prepared by the above procedure generally are reacted immediately with the sulfur intermediates which have been described above. Solvents may be included to facilitate the reaction, and alcohols have been found to be satisfactory solvents. The reaction between the sulfur intermediate and the dithiocarbamate salts generally is conducted at from ambient temperature to the reflux temperature of the mixture. The reaction is conducted until the reaction is completed which is generally from about

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5 to about 24 hours. At the end of the reaction, the aqueous phase is separated, and the product is recovered from the organic phase.

The product of the reaction of the sulfur monohalide with an olefinic hydrocarbon followed by reaction with the dithiocarbamate generally is a mixture of products which can be represented by the structural Formulae XVII or XVII-A. When the reaction is conducted with an aldehyde or a ketone in lieu of the olefinic hydrocarbon, the reaction product also is a mixture in which the major product is believed to be represented by the structural Formula XVII-B. It is not necessary to isolate the various products since the product mixtures are useful in lubricants and functional fluids.

The sulfur-coupled dithiocarbamates (C-3) also may be prepared by a process which comprises the steps of

(A) reacting an olefinic hydrocarbon with a halogen to produce a halogen-containing intermediate, and

(B) reacting said intermediate with an alkali metal sulfide and a salt of a dithiocarbamate in an amount sufficient to replace the halogen groups present partially with dithiocarbamate groups and/or partially with sulfide groups.

Any of the olefinic hydrocarbons and salts of dithiocarbamates described above may be utilized in this process. The reaction of a halogen with an olefinic hydrocarbon is well known in the art, and any procedure for effecting the reaction of a halogen with an olefinic hydrocarbon to produce a halogen-containing intermediate can be utilized.

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The alkali metal sulfide utilized in the second step may be generally represented by the structural formula

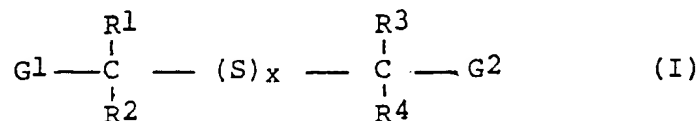


wherein M is an alkali metal and x is 1, 2 or 3. Sodium sulfide is preferred as the alkali metal sulfide for reasons of economy and effectiveness.

In one embodiment, the halogen-containing intermediate is reacted first with the alkali metal sulfide and then with the salt of a dithiocarbamate. Although the above reactants can be reacted at various ratios, it is generally desired to react four equivalents of the halogen-containing intermediate with one mole of the alkali metal sulfide and two moles of the dithiocarbamate salt. The reactions may be conducted at any convenient temperature such as from ambient temperature up to about 100°C or higher in some instances. The product obtained by this reaction generally will be a mixture which comprises primarily sulfur-coupled dithiocarbamates which are useful in lubricants and functional fluids.

Sulfur-Containing Compounds (C-4):

The sulfur compounds (C-4) which are useful in the compositions of the present invention are compounds characterized by the structural formula



wherein in Formula I, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each independently H or hydrocarbyl groups;

R<sup>1</sup> and/or R<sup>3</sup> may be G<sup>1</sup> or G<sup>2</sup>;

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R1 and R2 and/or R3 and R4 together may be alkylene groups containing about 4 to about 7 carbon atoms;

G1 and G2 are each independently C(X)R, COOR, C≡N, R<sup>5</sup>-C=NR<sup>6</sup>, CON(R)<sub>2</sub>, or NO<sub>2</sub>, and G1 may be CH<sub>2</sub>OH, wherein X is O or S, each of R and R<sup>5</sup> are independently H or a hydrocarbyl group, R<sup>6</sup> is H or a hydrocarbyl group;

when both G1 and G2 are R<sup>5</sup>C=NR<sup>6</sup>, the two R<sup>6</sup> groups together may be a hydrocarbylene group linking the two nitrogen atoms;

when G1 is CH<sub>2</sub>OH and G2 is COOR, a lactone may be formed by intramolecular combination of G1 and G2; and

x is a number from 1 to about 8.

R1, R2, R3 and R4 in Formula I are each independently hydrogen or hydrocarbyl groups. The hydrocarbyl groups may be aliphatic or aromatic groups such as alkyl, cycloalkyl, alkaryl, aralkyl or aryl groups. R1 and R2 and/or R3 and R4 together may be alkylene groups containing from about 4 to about 7 carbon atoms. In these embodiments, R1 and R2 together with the carbon atom bonded to R1 and R2 in Formula I will form a cycloalkyl group. Similarly, R3 and R4 together with the carbon atom bonded to R3 and R4 will form a cycloalkyl group. Also, R1 and/or R3 may be G1 or G2.

The hydrocarbyl groups R1, R2, R3 and R4 usually will contain up to about 30 carbon atoms. Preferably, the hydrocarbyl groups are alkyl groups containing up to about 10 carbon atoms. Specific examples of hydrocarbyl groups include methyl, ethyl, isopropyl, isobutyl, secondary butyl, cyclohexyl, cyclo-

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pentyl, octyl, dodecyl, octadecyl, eicosyl, behenyl, triacontonyl, phenyl, naphthyl, phenethyl, octyl-phenyl, tolyl, xylyl, dioctadecyl-phenyl, triethyl-phenyl, chloro-phenyl, methoxy-phenyl, dibromo-phenyl, nitro-phenyl, 3-chlorohexyl, etc.

The sulfur compounds (C-4) represented by Formula I may be thia-aldehydes or thia-ketones. That is, G1 and G2 in Formula I are C(O)R groups. Various thia-bisaldehyde compounds are known, and the synthesis of such compounds have been described in the prior art such as in U.S. Patents 3,296,137 and 2,580,695. Thia-aldehydes and thia-ketones are most conveniently prepared by the sulfurization of a suitable aldehyde or ketone such as one having the structural formula



wherein R1 is hydrogen, hydrocarbyl groups or C(O)R, R2 is hydrogen or a hydrocarbyl group, and R is hydrogen or a hydrocarbyl group. In these instances, R3 and R4 in Formula I will be the same as R1 and R2, respectively, and both G1 and G2 are C(O)R groups. When R1 is C(O)R, the sulfurization product contains four C(O)R groups.

The sulfurization can be accomplished by reacting the aldehyde or ketone with a sulfur halide such as sulfur monochloride (i.e., S2Cl2), sulfur dichloride, sulfur monobromide, sulfur dibromide, and mixtures of sulfur halide with sulfur flowers in varying amounts.

The reaction of an aldehyde or ketone with a sulfur halide may be effected simply by mixing the two reactants at the desired temperature which may range

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from about  $-30^{\circ}\text{C}$  to about  $250^{\circ}\text{C}$  or higher. The preferred reaction temperature generally is within the range of from about  $10$  to about  $80^{\circ}\text{C}$ . The reaction may be carried out in the presence of a diluent or solvent such as benzene, naphtha, hexane, carbon tetrachloride, chloroform, mineral oil, etc. The diluent/solvent facilitates the control of the reaction temperature and a thorough mixing of the the reactants.

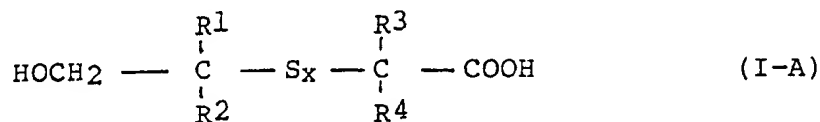
The relative amounts of the aldehyde or ketone and the sulfur halide may vary over wide ranges. In most instances, the reaction involves two moles of the aldehyde or ketone and one mole of the sulfur halide. In other instances, an excess of either one of the reactants may be used. When sulfur compounds are desired which contain more than two sulfur atoms, (e.g.,  $x$  is an integer from 3-8) these compounds can be obtained by reacting the aldehydes with a mixture of sulfur halide and sulfur. Sulfurization products wherein  $G1$  and  $G2$  are different and may be obtained by sulfurizing mixtures of aldehydes and ketones or mixtures of ketones containing different  $\text{C(O)R}$  groups.

Specific examples of thia-aldehydes and thia-ketones include compounds as represented by Formula I wherein  $G1$  and  $G2$  are  $\text{C(O)R}$  groups,  $x$  is 1 to 4 and  $R1$ ,  $R2$ ,  $R3$ ,  $R4$  and  $R$  are as follows:

$R1$	$R2$	$R3$	$R4$	$R$
$\text{CH}_3$	$\text{H}$	$\text{CH}_3$	$\text{H}$	$\text{H}$
$\text{CH}_3$	$\text{CH}_3$	$\text{CH}_3$	$\text{CH}_3$	$\text{CH}_3$
$\text{C}_2\text{H}_5$	$\text{H}$	$\text{C}_2\text{H}_5$	$\text{H}$	$\text{H}$
$\text{CH}_3\text{C(O)-}$	$\text{H}$	$\text{CH}_3\text{C(O)-}$	$\text{H}$	$\text{CH}_3$
$\text{CH}_3\text{C(O)-}$	$\text{H}$	$\text{CH}_3\text{C(O)-}$	$\text{H}$	$\text{H}$
$\text{C}_2\text{H}_5$	$\text{C}_4\text{H}_{11}$	$\text{C}_2\text{H}_5$	$\text{C}_4\text{H}_{11}$	$\text{H}$

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The thia-aldehydes and thia-ketones which can be prepared as described above can be converted to derivatives containing other functional groups which are normally derivable therefrom. Thus, in some of the embodiments of the invention, a thia-aldehyde or thia-ketone is converted to a derivative through contemporaneous conversion of the aldehyde or ketone groups to other terminal groups by chemical reactants and/or reagents. In such reactions, the thia group ( $S_x$ ) and the  $R^1$ -  $R^4$  groups are inert and remain unchanged in the compound. For example, the thia-bisaldehydes can be converted to hydroxy-acid derivatives wherein one of the aldehyde groups ( $G^1$ ) is converted to a  $COOH$  group, and the other aldehyde group ( $G^2$ ) is converted to a  $CH_2OH$  group. The hydroxy-acid derivatives are obtainable most conveniently by treating the corresponding thia-bisaldehyde with an alkaline reagent such as an alkali metal hydroxide or alkaline earth metal hydroxide, preferably a dilute aqueous solution thereof containing from about 5 to about 50% by weight of the hydroxide in water. Such alkaline reagents may be sodium hydroxide, potassium hydroxide, lithium hydroxide, barium hydroxide, calcium hydroxide, strontium hydroxide, etc. The hydroxy-acid is isolated from the reaction mixture by acidification with a mineral acid such as hydrochloric acid. The hydroxy-acid derivatives of thia-bisaldehydes can be represented by Formula I-A below.



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wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and x are as previously defined. Specific examples of such hydroxy-acid derivatives include 6-hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoic acid (i.e., conforming to Formula I-A wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are methyl and x is 2); 6-hydroxy-2,2-diethyl-5-propyl-5-butyl-3,4-dithiahexanoic acid; 6-hydroxy-2,2,5,5-tetraethyl-3,4-dithiahexanoic acid; etc.

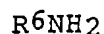
By virtue of the presence of the hydroxy group and the carboxylic group in the hydroxy-acids described by Formula I-A above, various other sulfur-containing compounds useful in the present invention can be obtained by the conversion of such hydroxy group and/or the carboxylic group to other polar groups normally derivable therefrom. Examples of such derivatives include esters formed by esterification of either or both of the hydroxy group and the carboxylic group; amides, imides, and acyl halides formed through the carboxylic group; and lactones formed through intramolecular cyclization of the hydroxy-acid accompanied with the elimination of water. The procedures for preparing such derivatives are well known to those skilled in the art, and it is not believed necessary to unduly lengthen the specification by including a detailed description of such procedures. More specifically, the carboxylic group (COOH) in Formula I-A can be converted to ester groups (COOR) and amide groups (CON(R)<sub>2</sub>) wherein the R groups may be hydrogen or hydrocarbyl groups containing from 1 to 30 carbon atoms and more generally from 1 to about 10 carbon atoms. Specific examples of such R groups include ethyl, propyl, butyl, phenyl, etc.

The procedures for preparing lactones through intramolecular cyclization of hydroxy-acids of Formula

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I-A accompanied by the elimination of water are well known in the art. Generally, the cyclization is promoted by the presence of materials such as acetic anhydride, and the reaction is effected by heating the mixtures to elevated temperatures such as the reflux temperature while removing volatile materials including water.

The sulfur compounds characterized by structural Formula I wherein G1 and/or G2 are  $R^5C=NR^6$  can be prepared from the corresponding thia-aldehydes and thia-ketones. These mono- and di-imine compounds are prepared by reacting one mole of the dialdehyde ( $C(O)H$ ) or diketone ( $C(O)R^5$ ) with one and two moles of an amine, respectively. The amines may be monoamines or polyamines. When polyamines are reacted with the thia-aldehydes or thia-ketones [ $-C(O)R^5$ ], cyclic di-imines can be formed. For example, when both G1 and G2 in Formula I are  $R^5C=NR^6$ , the two  $R^6$  groups together may be a hydrocarbylene group linking the two nitrogen atoms. The amines which are reacted with the thia-aldehydes and thia-ketones to form the imines may be characterized by the formula



wherein  $R^6$  is hydrogen, or hydrocarbyl, or an amino hydrocarbyl group. Generally, the hydrocarbyl groups will contain up to about 30 carbon atoms and will more often be aliphatic hydrocarbyl groups containing from 1 to about 30 carbon atoms.

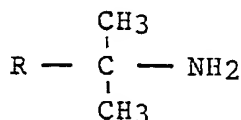
In one embodiment, the hydrocarbyl amines which are useful in preparing the imine derivatives of the present invention are primary hydrocarbyl amines contain-

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ing from about 2 to about 30 carbon atoms in the hydrocarbyl group, and more preferably from about 4 to about 20 carbon atoms in the hydrocarbyl group. The hydrocarbyl group may be saturated or unsaturated. Representative examples of primary saturated amines are the lower alkyl amines such as methyl amine, ethyl amine, n-propyl amine, n-butyl amine, n-amyl amine, n-hexyl amine; those known as aliphatic primary fatty amines and commercially known as "Armeen" primary amines (products available from Armak Chemicals, Chicago, Illinois). Typical fatty amines include alkyl amines such as n-hexylamine, n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-pentadecylamine, n-hexadecylamine, n-octadecylamine (stearyl amine), etc. These Armeen primary amines are available in both distilled and technical grades. While the distilled grade will provide a purer reaction product, the desirable amides, imines and imides will form in reactions with the amines of technical grade. Also suitable are mixed fatty amines such as Armak's Armeen-C, Armeen-O, Armeen-OL, Armeen-T, Armeen-HT, Armeen S and Armeen SD.

In another embodiment, the amine derived products of this invention are those derived from tertiary-aliphatic primary amines having at least about 4 carbon atoms in the alkyl group. For the most part, they are derived from alkyl amines having a total of less than about 30 carbon atoms in the alkyl group.

Usually the tertiary aliphatic primary amines are monoamines represented by the formula



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wherein R is a hydrocarbyl group containing from one to about 30 carbon atoms. Such amines are illustrated by tertiary-butyl amine, tertiary-hexyl primary amine, 1-methyl-1-amino-cyclohexane, tertiary-octyl primary amine, tertiary-decyl primary amine, tertiary-dodecyl primary amine, tertiary-tetradecyl primary amine, tertiary-hexadecyl primary amine, tertiary-octadecyl primary amine, tertiary-tetracosanyl primary amine, tertiary-octacosanyl primary amine.

Mixtures of amines are also useful for the purposes of this invention. Illustrative of amine mixtures of this type are "Primene 81R" which is a mixture of C11-C14 tertiary alkyl primary amines and "Primene JM-T" which is a similar mixture of C18-C22 tertiary alkyl primary amines (both are available from Rohm and Haas Company). The tertiary alkyl primary amines and methods for their preparation are well known to those of ordinary skill in the art and, therefore, further discussion is unnecessary. The tertiary alkyl primary amine useful for the purposes of this invention and methods for their preparation are described in U.S. Patent 2,945,749 which is hereby incorporated by reference for its teaching in this regard.

Primary amines in which the hydrocarbon chain comprises olefinic unsaturation also are useful. Thus, The R<sup>6</sup> group may contain one or more olefinic unsaturation depending on the length of the chain, usually no more than one double bond per 10 carbon atoms. Representative amines are dodecenylamine, myristoleylamine, palmitoleylamine, oleylamine and linoleylamine. Such unsaturated amines also are available under the Armeen tradename.

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The thia-aldehydes and thia-ketones also can be reacted with polyamines. Examples of useful polyamines include diamines such as mono- or dialkyl, symmetrical or asymmetrical ethylene diamines, propane diamines (1,2, or 1,3), and polyamine analogs of the above. Suitable commercial fatty polyamines are "Duomeen C" (N-coco-1,3-diaminopropane), "Duomeen S" (N-soya-1,3-diaminopropane), "Duomeen T" (N-tallow-1,3-diaminopropane), or "Duomeen O" (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available diamines described in Product Data Bulletin No. 7-10R1 of Armak Chemical Co., Chicago, Illinois.

The reaction of thia-aldehydes (and ketones) with primary amines or polyamines can be carried out by techniques well known to those skilled in the art. Generally, the thia-bisaldehyde or ketone is reacted with the amine or polyamine by reaction in a hydrocarbon solvent at an elevated temperature, generally in an atmosphere of nitrogen. As the reaction proceeds, the water which is formed is removed such as by distillation.

Sulfur compounds characterized by structural Formula I wherein G1 and G2 may be COOR, C=N and NO2 can be prepared by the reaction of compounds characterized by the structural formula



wherein R1 and R2 are as defined above, and G is COOR, C=N or NO2, or mixtures of different compound represented by Formula I-B with a sulfur halide or a

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mixture of sulfur halides and sulfur. Generally, about one mole of sulfur halide is reacted with about two moles of the compounds represented by Formula I-B. In one embodiment, R<sup>1</sup> also may be G. In such instances, the sulfur compounds which are formed as a result of the reaction with the sulfur halide will contain four G groups which may be the same or different depending upon the starting material. For example, when a di-ketone such as 2,4-pentanedione is reacted with sulfur monochloride, the resulting product contains four ketone groups; when the starting material contains a ketone group and an ester group (e.g., ethylacetoacetate), the resulting product contains two ketone groups and two ester groups; and when the starting material contains two ester groups (e.g., diethylmalonate), the product contains four ester groups. Other combinations of functional groups can be introduced into the sulfur products utilized in the present invention and represented by Formula I by selecting various starting materials containing the desired functional groups.

Sulfur compounds represented by Formula I wherein G<sup>1</sup> and/or G<sup>2</sup> are C≡N groups can be prepared by the reaction of compounds represented by Formula I-B wherein G is C≡N and R<sup>1</sup> and R<sup>2</sup> are hydrogen or hydrocarbyl groups. Preferably, R<sup>1</sup> is hydrogen and R<sup>2</sup> is a hydrocarbyl group. Examples of useful starting materials include, for example, propionitrile, butyronitrile, etc.

Compounds of Formula I wherein G<sup>1</sup> and G<sup>2</sup> are NO<sub>2</sub> groups can be prepared by (1) reacting a nitro hydrocarbon R<sup>1</sup>R<sup>2</sup>C(H)NO<sub>2</sub> with an alkali metal or alkaline earth metal alkoxide to form the salt of the nitro hydrocarbon, and (2) reacting said salt with

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sulfur monochloride in an inert, anhydrous nonhydroxylic medium to form a bis (1-nitrohydrocarbyl) disulfide. Preferably the nitro hydrocarbon is a primary nitro hydrocarbon (R1 is hydrogen and R2 is hydrocarbyl).

The starting primary nitro compounds used in carrying out this synthesis are well known. Illustrative compounds are nitroethane, 1-nitropropane, 1-nitrobutane, 1-nitro-4-methylhexane, (2-nitroethyl) benzene, etc.

The nature of the alkanol used in obtaining the alkali or alkaline earth metal salt of the starting primary nitro compound is not critical. It is only necessary that it be appropriate for reaction with the metal to form the alkoxide. Because they are easily obtainable and inexpensive, the lower alkanols (i.e., alkanols of 1 to 4 carbon atoms) such as methanol, ethanol and butanol will usually be employed in the synthesis.

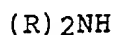
The medium in which the salt is reacted with  $S_2Cl_2$  must be inert to both the reactants. It is also essential that the medium be anhydrous and nonhydroxylic for the successful formation of the novel bis(1-nitrohydrocarbyl) disulfides. Examples of suitable media are ether, hexane, benzene, dioxane, higher alkyl ethers, etc.

Ordinarily, it is preferable to maintain a temperature of about 0-10°C during the preparation of the metal salt. However, temperatures from about 0 to 25°C may be used in this step of the process. In the preparation of the bisdisulfide temperatures in the range of -5 to +15°C may be used. Preferably, temperatures between about 0 to 5°C are used in this step of the process.

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The preparation of various thia-bisnitro compounds useful in the present invention is described in some detail in U.S. Patent 3,479,413, and the disclosure of this patent is hereby incorporated by reference. Representative examples of nitro sulfides useful in the present invention are: bis(1-nitro-2-phenylethyl) disulfide, bis(1-nitrodecyl) disulfide, bis(1-nitrododecyl) disulfide, bis(1-nitro-2-phenyldecyl) disulfide, bis(1-nitro-2-cyclohexylethyl) disulfide, bis(1-nitropentadecyl) disulfide, bis(1-nitro-3-cyclobutylpropyl) disulfide, bis(1-nitro-2-naphthylethyl) disulfide, bis(1-nitro-3-p-tolylpropyl) disulfide, bis(1-nitro-2-cyclooctylethyl) disulfide, and the like.

The carboxylic ester-containing sulfur compounds (i.e., Gl is COOR) described above can be utilized to prepare other sulfur compounds useful in the present invention. For example, the ester (COOR) can be hydrolyzed to the carboxylic acid (COOH) which can be converted to other esters by reaction with various alcohols or to amides by reaction with various amines including ammonia in primary or secondary amines such as those represented by the formula



wherein each R is hydrogen or a hydrocarbyl group. These hydrocarbyl groups may contain from 1 to about 30 carbon atoms and more generally will contain from about 1 to 10 carbon atoms.

As mentioned above, R1 and R2 and/or R3 and R4 together may be alkylene groups containing from about 4 to about 7 carbon atoms. In this embodiment, R1 and R2 (and R3 and R4) form a cyclic compound

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with the common carbon atom (i.e., the carbon atom which is common to R1 and R2 in Formula I. Such derivatives of structural Formula I can be prepared by reacting the appropriately substituted saturated cyclic material with sulfur halides as described above. Examples of such cyclic starting materials include cyclohexane carboxaldehyde ( $C_6H_{11}CHO$ ), cyclohexane carbonitrile ( $C_6H_{11}CN$ ), cyclohexane carboxamide ( $C_6H_{11}CONH_2$ ), cyclohexane carboxylic acid ( $C_6H_{11}COOH$ ), cyclobutane carboxylic acid ( $C_4H_7COOH$ ), cycloheptane carboxylic acid ( $C_7H_{13}COOH$ ), cycloheptyl cyanide ( $C_7H_{13}CN$ ), etc.

The following Example 1 illustrates the preparation of a sulfur composition represented by Formula I. Unless otherwise indicated in this example as well as throughout the specification and the appended claims, all parts and percentages are by weight, and all temperatures are in degrees centigrade.

#### Example 1

Sulfur monochloride (1620 parts, 12 moles) is charged to a 5-liter flask and warmed under nitrogen to a temperature of about  $53^\circ C$  whereupon 1766 parts (24.5 moles) of isobutyraldehyde are added dropwise under nitrogen at a temperature of about  $53-60^\circ C$  over a period of about 6.5 hours. After the addition of the isobutyraldehyde is completed, the mixture is heated slowly over a period of 6 hours to a temperature of about  $100^\circ C$  while blowing with nitrogen. The mixture is maintained at  $100^\circ C$  with nitrogen blowing for a period of about 6 hours and volatile materials are removed from the reaction vessel. The reaction product then is filtered through a filter aid, and the filtrate is the desired product containing 31.4% sulfur (theory, 31.08%). The

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desired reaction product, predominantly 2,2'-dithiodi-isobutyraldehyde, is recovered in about 95% yield.

Components (A), (B) and (C) of the inventive compositions can be mixed in any order using techniques known to those of ordinary skill in the art. Preferably, the relative weight ratios of components (A):(B):(C) in the compositions of the invention are generally about (1-500):(0.1-10):(1-500).

Lubricants and Functional Fluids:

The compositions of this invention are useful as additives for lubricants and functional fluids. These compositions can be employed in a wide variety of lubricants and functional fluids based on a wide variety of oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. These lubricants and functional fluids include crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines, and the like. They can also be used in gas engines, stationary power engines and turbines and the like. Transmission fluids (including both automatic transmission fluids and manual transmission fluids), transaxle lubricants, gear lubricants, metal-working lubricants, hydraulic fluids and other lubricating oil and grease compositions can also benefit from the incorporation therein of the compositions of the present invention.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as solvent-refined or acid-refined mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffin-naphthenic types. Oils of lubricating viscosity derived from coal

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or shale are also useful base oils. Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); alkyl benzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl) benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.); and the like.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having an average molecular weight of about 500-1000, diethyl ether of polypropylene glycol having an average molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3</sub>-C<sub>8</sub> fatty acid esters, or the C<sub>13</sub> oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl

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alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, pentaerythritol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)-sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, and the like.

Esters useful as synthetic oils also include those made from C5 to C12 monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of useful oils. These include tetraethyl-silicate, tetraisopropyl-silicate, tetra-(2-ethylhexyl)-silicate, tetra-(4-methylhexyl)-silicate, tetra(p-tert-butylphenyl)-silicate, hexyl-(4-methyl-2-pentoxo)-di-siloxane, poly(methyl)-siloxanes, poly-(methylphenyl)-siloxanes, etc. Other useful synthetic oils include liquid esters of phosphorus-containing acid (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans, and the like.

Unrefined, refined and rerefined oils (and mixtures of each with each other) of the type disclosed hereinabove can be used in the lubricant and functional fluid compositions of the present invention. Unrefined oils are those obtained directly from a natural or

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synthetic source without further purification treatment. For example, a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except that they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those of skill in the art such as solvent extraction, distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed toward removal of spent additives and oil breakdown products.

Generally, the lubricants and functional fluids of the present invention contain an effective amount of the composition of this invention sufficient to provide said lubricants and functional fluids with improved anti-wear, load-carrying, extreme pressure (E.P.), and/or corrosion-inhibiting properties. Normally the compositions of the present invention will be employed in such lubricants and functional fluids at a level in the range of about 0.02% to about 20% by weight, preferably about 0.05% to about 5% by weight of the total weight of the lubricant or functional fluid. Preferably, component (A) is employed at a concentration in the range of about 0.01% to about 5%, more preferably about 0.01% to about 2%, more preferably about 0.01% to about 1% by weight based on the total weight of the

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lubricant or functional fluid. Component (B) is preferably employed at a concentration in the range of about 0.001% to about 0.1% by weight based on the total weight of the lubricant or functional fluid. Component (C) is preferably employed at a concentration in the range of about 0.01% to about 5% by weight based on the total weight of the lubricant or functional fluid.

The invention also contemplates the use of lubricants and functional fluids containing other additives in addition to the compositions of this invention. Such additives include, for example, ashless detergents and dispersants, corrosion-inhibiting agents, antioxidants, viscosity improving agents, E.P. agents, pour point depressants, color stabilizers, anti-foam agents, etc.

Ashless detergents and dispersants are so called despite the fact that, depending on its constitution, the dispersant may upon combustion yield a non-volatile material such as boric oxide or phosphorus pentoxide; however, it does not ordinarily contain metal and therefore does not yield a metal-containing ash on combustion. Many types are known in the art, and any of them are suitable for use in the lubricants of this invention. The following are illustrative:

(1) Reaction products of carboxylic acids (or derivatives thereof) containing at least about 34 and preferably at least about 54 carbon atoms with nitrogen containing compounds such as amine, organic hydroxy compounds such as phenols and alcohols, and/or basic inorganic materials. Examples of these "carboxylic dispersants" are described in British Patent 1,306,529 and in many U.S. Patents including the following:

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3,163,603	3,351,552	3,541,012
3,184,474	3,381,022	3,543,678
3,215,707	3,399,141	3,542,680
3,219,666	3,415,750	3,567,637
3,271,310	3,433,744	3,574,101
3,272,746	3,444,170	3,576,743
3,281,357	3,448,048	3,630,904
3,306,908	3,448,049	3,632,510
3,311,558	3,451,933	3,632,511
3,316,177	3,454,607	3,697,428
3,340,281	3,467,668	3,725,441
3,341,542	3,501,405	4,234,435
3,346,493	3,522,179	Re 26,433

(2) Reaction products of relatively high molecular weight aliphatic or alicyclic halides with amines, preferably oxyalkylene polyamines. These may be characterized as "amine dispersants" and examples thereof are described for example, in the following U.S. Patents:

3,275,554	3,454,555
3,438,757	3,565,804

(3) Reaction products of alkyl phenols in which the alkyl group contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), which may be characterized as "Mannich dispersants". The materials described in the following U.S. Patents are illustrative:

2,459,112	3,442,808	3,591,598
2,962,442	3,448,047	3,600,372
2,984,550	3,454,497	3,634,515
3,036,003	3,459,661	3,649,229
3,166,516	3,461,172	3,697,574
3,236,770	3,493,520	3,725,277

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3,355,270	3,539,633	3,725,480
3,368,972	3,558,743	3,726,882
3,413,347	3,586,629	3,980,569

(4) Products obtained by post-treating the carboxylic, amine or Mannich dispersants with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. Patents:

3,036,003	3,282,955	3,493,520	3,639,242
3,087,936	3,312,619	3,502,677	3,649,229
3,200,107	3,366,569	3,513,093	3,649,659
3,216,936	3,367,943	3,533,945	3,658,836
3,254,025	3,373,111	3,539,633	3,697,574
3,256,185	3,403,102	3,573,010	3,702,757
3,278,550	3,442,808	3,579,450	3,703,536
3,280,234	3,455,831	3,591,598	3,704,308
3,281,428	3,455,832	3,600,372	3,708,422

(5) Interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. These may be characterized as "polymeric dispersants" and examples thereof are disclosed in the following U.S. Patents:

3,329,658	3,666,730
3,449,250	3,687,849
3,519,565	3,702,300

The above-noted patents are incorporated by reference herein for their disclosures of ashless dispersants.

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Extreme pressure (E.P.) agents, corrosion-inhibiting agents and antioxidants which may be included in the lubricants and functional fluids of the invention are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl)disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, and sulfurized terpene; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate, phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, diisobutyl-substituted phenyl phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)-phosphorodithioate, cadmium dinonylphosphorodithioate, and the zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

Many of the above-mentioned extreme pressure agents, corrosion inhibitors and antioxidants also serve as antiwear agents. Zinc dialkylphosphorodithioates are a well known example.

Pour point depressants are a particularly useful type of additive often included in the lubricants

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and functional fluids described herein. The use of such pour point depressants in oil-based compositions to improve low temperature properties of oil-based compositions is well known in the art. See, for example, page 8 of "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith (Lezius-Hiles Co. publishers, Cleveland, Ohio, 1967), which is incorporated herein by reference.

Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 which are hereby incorporated by reference.

Anti-foam agents are used to reduce or prevent the formation of stable foam. Typical anti-foam agents include silicones or organic polymers. Additional anti-foam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162, which are incorporated herein by reference.

Components (A), (B) and (C) of the compositions of this invention can be added directly to the lubricant or functional fluid. Preferably, however, they are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually contain from about 10% to about 90% by weight of the inventive compositions and

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may contain, in addition, one or more other additives known in the art or described hereinabove. The remainder of the concentrate is the substantially inert normally liquid diluent.

Examples of hydraulic fluids within the scope of the invention are as follows (all numerical values being parts by weight):

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	<u>A</u>	<u>B</u>	<u>C</u>
Phosphorus-containing amide derived from di(isooctyl) phosphorodithioic acid, acryl- amide and paraformaldehyde. (Antiwear Agent)	0.172	0.172	-----
Phosphorus-containing ester derived from the reaction of O,O-di(alkyl) phosphorodithioic acid containing 65% isobutyl groups and 35% amyl groups and methylacrylate, post-treated with propylene oxide. (Antiwear Agent)	0.517	0.517	0.50
Dibutyl hydrogen phosphite (Antiwear Agent)	-----	-----	-----
Thiophosphate ester (Antiwear Agent)	-----	-----	-----
Dithiocarbamate derived from reaction of butylamine, carbon disulfide and methyl acrylate (Antiwear Agent)	-----	-----	-----
Methylene-coupled dithiocarbam- ate derived from diamylamine, carbon disulfide, sodium hydrox- ide and methylene chloride (Antiwear Agent)	-----	-----	-----
Sulfur-containing compound prepared from sulfur monochlor- ide and isobutyraldehyde as in Ex. 1 (Antiwear Agent)	-----	-----	0.17
Oxidation Inhibitor	0.43	0.43	0.38
Rust Inhibitor	0.043	0.03	0.04
Demulsifier	0.006	0.014	0.007
Tolyltriazole (Metal Deactivator)	-----	-----	0.005

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	<u>A</u>	<u>B</u>	<u>C</u>
Benzotriazole (Metal Deactivator)	-----	-----	-----
Alkylated Triazole (Metal Deactivator)	0.0093	0.00465	-----
300 Conversion Calcium Phenate (Detergent)	0.15	-----	-----
2000 Conversion Calcium Sul- fonate (Detergent)	-----	0.10	-----
700 Conversion Magnesium Sul- fonate (Detergent)	-----	-----	0.15
700 Conversion Magnesium Sal- icylate (Detergent)	-----	-----	-----
2600 Conversion Sodium Sul- fonate (Detergent)	-----	-----	0.05
Diluent Oil	98.67	98.73	98.70

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	<u>D</u>	<u>E</u>	<u>F</u>
Phosphorus-containing amide derived from di(isooctyl) phosphorodithioic acid, acryl- amide and paraformaldehyde. (Antiwear Agent)	-----	0.172	0.172
Phosphorus-containing ester derived from the reaction of O,O-di(alkyl) phosphorodithioic acid containing 65% isobutyl groups and 35% amyl groups and methylacrylate, post-treated with propylene oxide. (Antiwear Agent)	0.50	0.48	0.50
Dibutyl hydrogen phosphite (Antiwear Agent)	-----	-----	-----
Thiophosphate ester (Antiwear Agent)	-----	-----	-----
Dithiocarbamate derived from reaction of butylamine, carbon disulfide and methyl acrylate (Antiwear Agent)	-----	-----	-----
Methylene-coupled dithiocarbam- ate derived from diamylamine, carbon disulfide, sodium hydrox- ide and methylene chloride (Antiwear Agent)	0.17	-----	-----
Sulfur-containing compound prepared from sulfur monochlor- ide and isobutyraldehyde as in Ex. 1 (Antiwear Agent)	-----	-----	-----
Oxidation Inhibitor	0.38	0.40	0.38
Rust Inhibitor	0.04	0.043	0.04
Demulsifier	0.007	0.006	0.014
Tolyltriazole (Metal Deactivator)	0.005	0.0093	0.01

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	<u>D</u>	<u>E</u>	<u>F</u>
Benzotriazole (Metal Deactivator)	-----	-----	-----
Alkylated Triazole (Metal Deactivator)	-----	-----	-----
300 Conversion Calcium Phenate (Detergent)	-----	-----	0.025
2000 Conversion Calcium Sul- fonate (Detergent)	0.05	-----	-----
700 Conversion Magnesium Sul- fonate (Detergent)	-----	-----	0.05
700 Conversion Magnesium Sal- icylate (Detergent)	-----	0.075	-----
2600 Conversion Sodium Sul- fonate (Detergent)	0.15	-----	-----
Diluent Oil	98.70	98.81	98.81

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	<u>G</u>	<u>H</u>	<u>I</u>
Phosphorus-containing amide derived from di(isooctyl) phosphorodithioic acid, acryl- amide and paraformaldehyde. (Antiwear Agent)	0.17	-----	-----
Phosphorus-containing ester derived from the reaction of O,O-di(alkyl) phosphorodithioic acid containing 65% isobutyl groups and 35% amyl groups and methylacrylate, post-treated with propylene oxide. (Antiwear Agent)	0.48	-----	-----
Dibutyl hydrogen phosphite (Antiwear Agent)	-----	-----	-----
Thiophosphate ester (Antiwear Agent)	-----	-----	-----
Dithiocarbamate derived from reaction of butylamine, carbon disulfide and methyl acrylate (Antiwear Agent)	-----	-----	-----
Methylene-coupled dithiocarbam- ate derived from diamylamine, carbon disulfide, sodium hydrox- ide and methylene chloride (Antiwear Agent)	-----	0.50	0.50
Sulfur-containing compound prepared from sulfur monochlor- ide and isobutyraldehyde as in Ex. 1 (Antiwear Agent)	-----	-----	0.17
Oxidation Inhibitor	0.40	0.40	0.43
Rust Inhibitor	0.05	0.04	0.05
Demulsifier	0.006	0.014	0.007
Tolyltriazole (Metal Deactivator)	-----	-----	-----

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	<u>G</u>	<u>H</u>	<u>I</u>
Benzotriazole (Metal Deactivator)	0.005	0.005	-----
Alkylated Triazole (Metal Deactivator)	-----	-----	0.01
300 Conversion Calcium Phenate (Detergent)	-----	0.025	-----
2000 Conversion Calcium Sul- fonate (Detergent)	0.05	-----	0.10
700 Conversion Magnesium Sul- fonate (Detergent)	-----	-----	-----
700 Conversion Magnesium Sal- icylate (Detergent)	-----	0.05	0.05
2600 Conversion Sodium Sul- fonate (Detergent)	0.025	-----	-----
Diluent Oil	98.81	98.97	98.68

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	<u>J</u>	<u>K</u>	<u>L</u>
Phosphorus-containing amide derived from di(isooctyl) phosphorodithioic acid, acryl- amide and paraformaldehyde. (Antiwear Agent)	0.10	0.10	0.50
Phosphorus-containing ester derived from the reaction of O,O-di(alkyl) phosphorodithioic acid containing 65% isobutyl groups and 35% amyl groups and methylacrylate, post-treated with propylene oxide. (Antiwear Agent)	0.50	0.50	-----
Dibutyl hydrogen phosphite (Antiwear Agent)	-----	-----	-----
Thiophosphate ester (Antiwear Agent)	-----	-----	-----
Dithiocarbamate derived from reaction of butylamine, carbon disulfide and methyl acrylate (Antiwear Agent)	-----	-----	-----
Methylene-coupled dithiocarbam- ate derived from diamylamine, carbon disulfide, sodium hydrox- ide and methylene chloride (Antiwear Agent)	0.07	-----	0.10
Sulfur-containing compound prepared from sulfur monochlor- ide and isobutyraldehyde as in Ex. 1 (Antiwear Agent)	-----	0.07	0.07
Oxidation Inhibitor	0.38	0.40	0.43
Rust Inhibitor	0.04	0.043	0.05
Demulsifier	0.006	0.014	0.007
Tolyltriazole (Metal Deactivator)	0.01	-----	0.025

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	<u>J</u>	<u>K</u>	<u>L</u>
Benzotriazole (Metal Deactivator)	-----	0.005	-----
Alkylated Triazole (Metal Deactivator)	-----	-----	-----
300 Conversion Calcium Phenate (Detergent)	0.05	-----	-----
2000 Conversion Calcium Sul- fonate (Detergent)	-----	-----	0.10
700 Conversion Magnesium Sul- fonate (Detergent)	0.10	-----	-----
700 Conversion Magnesium Sal- icylate (Detergent)	-----	0.075	-----
2600 Conversion Sodium Sul- fonate (Detergent)	-----	-----	0.05
Diluent Oil	98.74	98.79	98.67

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	<u>M</u>	<u>N</u>	<u>O</u>
2 Phosphorus-containing amide derived from di(isooctyl) phosphorodithioic acid, acryl- amide and paraformaldehyde. 3 (Antiwear Agent)	-----	-----	-----
Phosphorus-containing ester derived from the reaction of O,O-di(alkyl) phosphorodithioic acid containing 65% isobutyl groups and 35% amyl groups and methylacrylate, post-treated with propylene oxide. (Antiwear Agent)	0.50	0.50	-----
Dibutyl hydrogen phosphite (Antiwear Agent)	0.10	-----	-----
Thiophosphate ester (Antiwear Agent)	-----	0.10	-----
Dithiocarbamate derived from reaction of butylamine, carbon disulfide and methyl acrylate (Antiwear Agent)	-----	-----	0.60
Methylene-coupled dithiocarbam- ate derived from diamylamine, carbon disulfide, sodium hydrox- ide and methylene chloride (Antiwear Agent)	-----	-----	-----
Sulfur-containing compound prepared from sulfur monochlor- ide and isobutyraldehyde as in Ex. 1 (Antiwear Agent)	-----	-----	-----
4 Oxidation Inhibitor	0.50	0.50	0.50
5 Rust Inhibitor	0.05	0.05	0.05
Demulsifier	-----	-----	-----
Tolyltriazole (Metal Deactivator)	0.01	-----	-----

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	<u>M</u>	<u>N</u>	<u>O</u>
Benzotriazole (Metal Deactivator)	-----	-----	-----
Alkylated Triazole (Metal Deactivator)	0.01	0.01	0.04
300 Conversion Calcium Phenate (Detergent)	-----	0.40	-----
2000 Conversion Calcium Sul- fonate (Detergent)	-----	-----	-----
700 Conversion Magnesium Sul- fonate (Detergent)	-----	-----	-----
700 Conversion Magnesium Sal- icylate (Detergent)	0.05	-----	0.25
2600 Conversion Sodium Sul- fonate (Detergent)	-----	-----	-----
Diluent Oil	98.78	98.44	98.56

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The lubricant compositions of the present invention may be in the form of greases in which any of the above-described oils of lubricating viscosity can be employed as a vehicle. Where the lubricant is to be used in the form of a grease, the lubricating oil generally is employed in an amount sufficient to balance the total grease composition and generally, the grease compositions will contain various quantities of thickening agents and other additive components to provide desirable properties.

A wide variety of thickening agents can be used in the preparation of the greases of this invention. Included among the thickening agents are alkali and alkaline earth metal soaps of fatty acids and fatty materials having from about 12 to about 30 carbon atoms. The metals are typified by sodium, lithium, calcium and barium. Examples of fatty materials include stearic acid, hydroxy stearic acid, stearin, oleic acid, palmitic acid, myristic acid, cottonseed oil acids, and hydrogenated fish oils.

Other thickening agents include salt and salt-soap complexes as calcium stearate-acetate (U.S. Patent 2,197,263), barium stearate acetate (U.S. Patent 2,564,561), calcium stearate-caprylate-acetate complexes (U.S. Patent 2,999,065), calcium caprylate-acetate (U.S. Patent 2,999,066), and calcium salts and soaps of low-, intermediate- and high-molecular weight acids and of nut oil acids.

Particularly useful thickening agents employed in the grease compositions are essentially hydrophilic in character, but which have been converted into a hydrophobic condition by the introduction of long chain hydrocarbon radicals onto the surface of the clay parti-

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cles prior to their use as a component of a grease composition, as, for example, by being subjected to a preliminary treatment with an organic cationic surface-active agent, such as an onium compound. Typical onium compounds are tetraalkylammonium chlorides, such as dimethyl dioctadecyl ammonium chloride, dimethyl dibenzyl ammonium chloride and mixtures thereof. This method of conversion, being well known to those skilled in the art, and is believed to require no further discussion. More specifically, the clays which are useful as starting materials in forming the thickening agents to be employed in the grease compositions, can comprise the naturally occurring chemically unmodified clays. These clays are crystalline complex silicates, the exact composition of which is not subject to precise description, since they vary widely from one natural source to another. These clays can be described as complex inorganic silicates such as aluminum silicates, magnesium silicates, barium silicates, and the like, containing, in addition to the silicate lattice, varying amounts of cation-exchangeable groups such as sodium. Hydrophilic clays which are particularly useful for conversion to desired thickening agents include montmorillonite clays, such as bentonite, attapulgite, hectorite, illite, saponite, sepiolite, biotite, vermiculite, zeolite clays, and the like. The thickening agent is employed in an amount from about 0.5 to about 30, and preferably from 3% to 15% by weight of the total grease composition.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that

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the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

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Claims

1. A composition comprising:

(A) at least one neutral or basic metal salt or boron-containing neutral or basic metal salt of at least one acidic organic compound, the metal in said salt being selected from the group consisting of alkali metals, alkaline-earth metals, zinc, copper, aluminum or a mixture of two or more of said metals;

(B) at least one metal deactivator; and

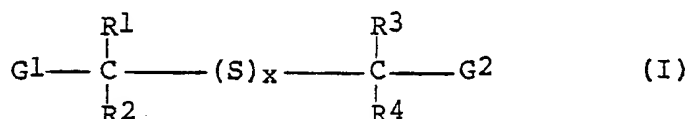
(C) at least one compound selected from the group consisting of

(C-1) phosphorus-containing amide;

(C-2) phosphorus-containing ester;

(C-3) sulfur-coupled dithiocarbamate;

(C-4) sulfur-containing compound represented by the formula



wherein in Formula I:

R1, R2, R3 and R4 are each independently H or hydrocarbyl groups;

R1 and/or R3 may be G1 or G2;

R1 and R2 and/or R3 and R4 together may be alkylene groups containing about 4 to about 7 carbon atoms;

G1 and G2 are each independently C(X)R, COOR, C≡N, R<sup>5</sup>-C=NR<sup>6</sup>, CON(R)<sub>2</sub> or NO<sub>2</sub>, and G1 also may be CH<sub>2</sub>OH, wherein X is O or S, each of R and R<sup>5</sup> are independently H or a hydrocarbyl group, R<sup>6</sup> is H or a hydrocarbyl group;

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when both G<sup>1</sup> and G<sup>2</sup> are R<sup>5</sup>C=NR<sup>6</sup>, the two R<sup>6</sup> groups together may be a hydrocarbylene group linking the two nitrogen atoms;

when G<sup>1</sup> is CH<sub>2</sub>OH and G<sup>2</sup> is COOR, a lactone may be formed by intramolecular condensation of G<sup>1</sup> and G<sup>2</sup>; and

x is an integer from 1 to about 8; and

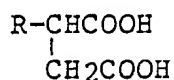
(C-5) mixture of two or more of any of (C-1) to (C-4).

2. The composition of claim 1 wherein said acidic organic compound comprises at least one carboxylic acid, sulfur-containing acid, phosphorus-containing acid, phenol or mixture of two or more thereof.

3. The composition of claim 1 wherein said acidic organic compound comprises at least one aliphatic, cycloaliphatic or aromatic carboxylic acid.

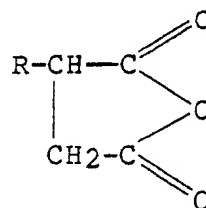
4. The composition of claim 1 wherein said acidic organic compound comprises at least one monocarboxylic acid, polycarboxylic acid or mixture thereof.

5. The composition of claim 1 wherein said acidic organic compound comprises at least one compound represented by the formula



(II)

or

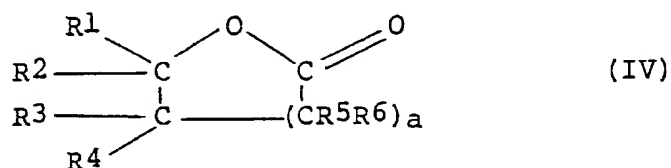


(III)

wherein in Formulae II and III, R is a hydrocarbyl group.

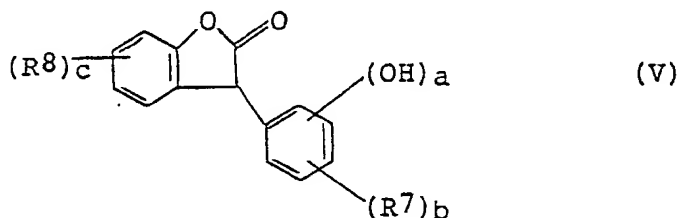
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6. The composition of claim 1 wherein said acidic organic compound is represented by the formula



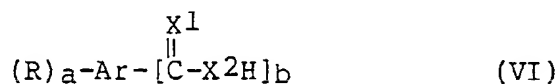
wherein in Formula IV, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are independently H or hydrocarbonyl groups; R<sup>2</sup> and R<sup>3</sup> can be linked together to form an aliphatic or aromatic ring; and a is a number in the range of zero to about 4.

7. The composition of claim 1 wherein said acidic organic compound is represented by the formula



wherein in Formula V, R<sup>7</sup> and R<sup>8</sup> are aliphatic hydrocarbyl groups, a and b are numbers in the range of zero to 5 with the proviso that the sum of a and b does not exceed 5, c is a number in the range of zero to 4.

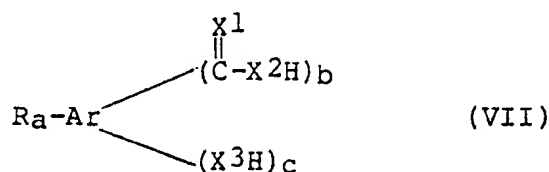
8. The composition of claim 1 wherein said acidic organic compound comprises at least one compound represented by the formula



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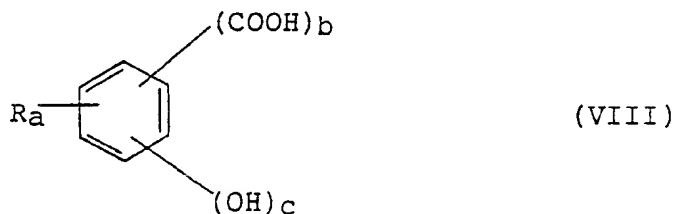
wherein in Formula VI, R is an aliphatic hydrocarbyl group, Ar is an aromatic group, X1 and X2 are independently oxygen or sulfur, a is a number in the range of zero to about 4, and b is a number in the range of 1 to about 4 with the proviso that the sum of a and b does not exceed the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar.

9. The composition of claim 1 wherein said acidic organic compound comprises at least one compound represented by the formula



wherein in Formula VII, R is an aliphatic hydrocarbyl group; Ar is an aromatic group; X1, X2 and X3 are independently oxygen or sulfur; a is a number in the range of zero to about 4; b is a number in the range of 1 to about 4; and c is a number in the range of 1 to about 4; with the proviso that the sum of a, b and c does not exceed the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar.

10. The composition of claim 1 wherein said acidic organic compound comprises at least one compound represented by the formula



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wherein in Formula VIII, R is an aliphatic hydrocarbyl group, a is a number in the range of zero to about 4, b is a number in the range of 1 to about 4, c is a number in the range of 1 to about 4, with the proviso that the sum of a, b and c does not exceed 6.

11. The composition of claim 1 wherein said acidic organic compound comprises a salicylic acid.

12. The composition of claim 1 wherein said acidic organic compound is a sulfonic acid, sulfamic acid, thiosulfonic acid, sulfinic acid, sulfenic acid, partial ester sulfuric acid, sulfurous acid or thio-sulfuric acid.

13. The composition of claim 1 wherein said acidic organic compound comprises at least one compound represented by the formula



wherein in Formula IX, R1 is an aliphatic hydrocarbyl group, T is a cyclic hydrocarbyl group, a is at least 1, and b is at least 1.

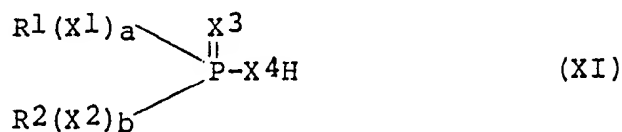
14. The composition of claim 1 wherein said acidic organic compound comprises at least one compound represented by the formula



wherein in Formula X, R2 is an aliphatic hydrocarbyl group, and a is at least 1.

15. The composition of claim 1 wherein said acidic organic compound comprises at least one compound represented by the formula

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wherein in Formula XI,  $\text{X}^1$ ,  $\text{X}^2$  and  $\text{X}^3$  and  $\text{X}^4$  are independently oxygen or sulfur,  $a$  and  $b$  are independently zero or 1, and  $\text{R}^1$  and  $\text{R}^2$  are independently hydrocarbyl groups.

16. The composition of claim 15 wherein in Formula XI,  $\text{X}^1$  and  $\text{X}^2$  are oxygen.

17. The composition of claim 15 wherein in Formula XI,  $\text{X}^3$  and  $\text{X}^4$  are sulfur.

18. The composition of claim 15 wherein in Formula XI,  $\text{R}^1$  and  $\text{R}^2$  are independently hydrocarbyl groups of from 1 to about 50 carbon atoms.

19. The composition of claim 15 wherein in Formula XI,  $\text{R}^1$  and  $\text{R}^2$  are independently *t*-butyl, isobutyl, amyl, isooctyl, decyl, dodecyl, eicosyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylphenyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl or alkylphenylalkyl groups.

20. The composition of claim 1 wherein said acidic organic compound comprises at least one compound represented by the formula



wherein in Formula XII,  $\text{R}$  is a hydrocarbyl group of about 4 to about 400 carbon atoms,  $\text{Ar}$  is an aromatic group,  $a$  and  $b$  are numbers each being at least one, the sum of  $a$  and  $b$  ranging from 2 up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of  $\text{Ar}$ .

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21. The composition of claim 20 wherein in Formula XII, R and a are such that there is an average of at least about 8 aliphatic carbon atoms provided by the R groups for each phenol molecule represented by Formula XII.

22. The composition of claim 20 wherein Ar in Formula XII is a benzene nucleus, lower alkylene bridged benzene nucleus or a naphthalene nucleus.

23. The composition of claim 1 wherein the metal in said salt (A) is selected from the group consisting of lithium, sodium, magnesium, calcium, potassium, barium, aluminum, zinc, copper or a mixture of two or more thereof.

24. The composition of claim 1 wherein the metal in said salt (A) is selected from the group consisting of sodium, magnesium, calcium or a mixture of two or more thereof.

25. The composition of claim 1 wherein component (A) is a boron-containing neutral or basic metal salt prepared by the process comprising reacting

(1) at least one acidic organic compound or precursor thereof;

(2) at least one metal-containing compound selected from the group consisting of alkali metals, alkaline earth metals, zinc, copper, aluminum or a mixture of two or more thereof;

(3) at least one boron compound; and

(4) at least one promoter.

26. The composition of claim 1 wherein component (A) has from about 100% to about 4000% of the metal present in the corresponding neutral salt.

27. The composition of claim 1 wherein component (A) comprises a magnesium sulfonate, a sodium sulfonate or a mixture thereof.

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28. The composition of claim 1 wherein component (A) comprises a magnesium salicylate.

29. The composition of claim 1 wherein component (B) comprises benzotriazole; an alkyl-, aryl-, alkaryl- or arylalk-substituted benzotriazole; a hydroxy-, alkoxy-, halo-, nitro-, carboxy- or carbalkoxy-substituted benzotriazole; or a mixture of two or more thereof.

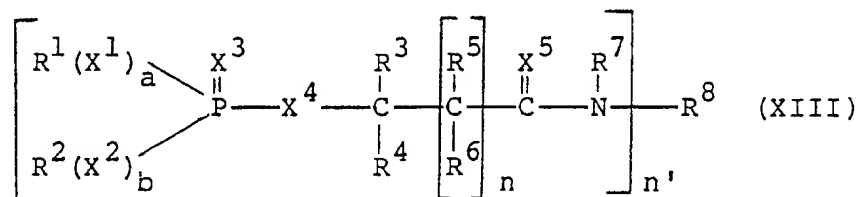
30. The composition of claim 1 wherein component (B) comprises benzotriazole.

31. The composition of claim 1 wherein component (B) comprises tolyltriazole.

32. The composition of claim 1 wherein component (B) comprises the reaction product of at least one benzotriazole and at least one amine.

33. The composition of claim 1 wherein component (B) comprises the reaction product of at least one benzotriazole and at least one nitrogen-containing ashless dispersant.

34. The composition of claim 1 wherein component (C-1) comprises at least one compound represented by the formula:



wherein in Formula XIII,  $X^1$ ,  $X^2$ ,  $X^3$ ,  $X^4$  and  $X^5$  are independently oxygen or sulfur;

$R^1$  and  $R^2$  are independently hydrocarbyl groups;

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R3, R4, R5, R6 and R7 are independently hydrogen, halogen or hydrocarbyl groups;

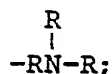
a and b independently are zero or 1;

n is zero or 1;

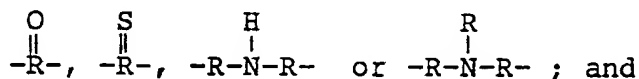
n' is 1, 2 or 3;

with the proviso that:

(1) when n' is 1, R8 is hydrogen, -R, -ROH, -ROR, -RSR or



(2) when n' is 2, R8 is a coupling group selected from -R-, -R\*- , -R-O-R-, -R-S-R-,



(3) when n' is 3, R8 is the coupling group

$$\begin{array}{c} -\text{R}-\text{N}-\text{R}- \\ | \\ \text{R} \\ | \end{array}$$

wherein each R is independently a hydrocarbyl group of 1 to about 12 carbon atoms; and R\* is a hydrocarbyl or carboxyhydrocarbyl group of 1 to about 60 carbon atoms.

35. The composition of claim 34 wherein in Formula XIII, X1 and X2 are oxygen.

36. The composition of claim 34 wherein in Formula XIII, X3 and X4 are sulfur.

37. The composition of claim 34 wherein X5 is oxygen.

38. The composition of claim 34 wherein in Formula XIII, R1 and R2 are independently hydrocarbyl groups of from 1 to about 50 carbon atoms.

39. The composition of claim 34 wherein in Formula XIII, R1 and R2 are independently t-butyl,

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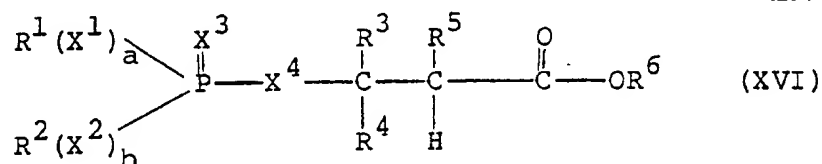
isobutyl, amyl, isooctyl, decyl, dodecyl, eicosyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylnaphthyl, phenylalkyl, naphthylalkyl, alkylphenyl-alkyl or alkylnaphthylalkyl groups.

40. The composition of claim 34 wherein in Formula XIII, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently hydrogen or hydrocarbyl groups of from 1 to about 50 carbon atoms.

41. The composition of claim 34 wherein in Formula XIII, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently hydrogen; alkyl groups of from 1 to about 22 carbon atoms; cycloalkyl groups of from about 4 to about 22 carbon atoms; or aromatic, alkyl-substituted aromatic or aromatic-substituted alkyl groups of from about 4 to about 34 carbon atoms.

42. The composition of claim 34 wherein in Formula XIII, n' is 2 and R<sup>8</sup> is -CH<sub>2</sub>-O-CH<sub>2</sub>-.

43. The composition of claim 1 wherein component (C-2) comprises at least one compound represented by the formula:



wherein in Formula XVI, X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup> and X<sup>4</sup> are independently oxygen or sulfur;

R<sup>1</sup> and R<sup>2</sup> are independently hydrocarbyl groups;

R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are independently hydrogen or hydrocarbyl groups;

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R<sub>6</sub> is a hydrocarbyl group; and  
a and b are independently zero or 1.

44. The composition of claim 43 wherein in Formula XVI, X<sub>1</sub> and X<sub>2</sub> are oxygen.

45. The composition of claim 43 wherein in Formula XVI, X<sub>3</sub> and X<sub>4</sub> are sulfur.

46. The composition of claim 43 wherein in Formula XVI, R<sub>1</sub> and R<sub>2</sub> are independently hydrocarbyl groups of from 1 to about 50 carbon atoms.

47. The composition of claim 43 wherein in Formula XVI, R<sub>1</sub> and R<sub>2</sub> independently are t-butyl, isobutyl, amyl, isooctyl, decyl, dodecyl, eicosyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylphenyl, phenylalkyl, naphthylalkyl, alkylphenyl-alkyl or alkylphenylalkyl groups.

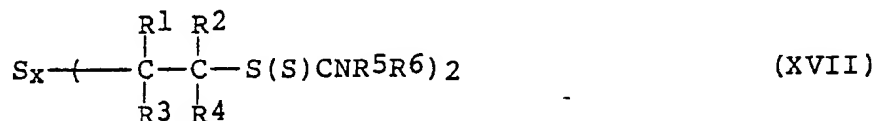
48. The composition of claim 43 wherein in Formula XVI, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are independently hydrogen or hydrocarbyl groups of from 1 to about 50 carbon atoms.

49. The composition of claim 43 wherein in Formula XVI, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are independently hydrogen; alkyl groups of from 1 to about 22 carbon atoms; cycloalkyl groups of from about 4 to about 22 carbon atoms; or aromatic, alkyl-substituted aromatic or aromatic-substituted alkyl groups of from about 4 to about 34 carbon atoms.

50. The composition of claim 43 wherein in Formula XVI, R<sub>6</sub> is an alkyl group of from 1 to about 22 carbon atoms; a cycloalkyl group of from about 4 to about 22 carbon atoms; or an aromatic, alkyl-substituted aromatic or aromatic-substituted alkyl group of from about 4 to about 34 carbon atoms.

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51. The composition of claim 1 wherein component (C-3) is represented by the formula



wherein in Formula XVII, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> is independently H or a hydrocarbyl group; R<sub>4</sub> is H, OH or a hydrocarbyl group; R<sub>5</sub> and R<sub>6</sub> are independently H, hydrocarbyl, or hydroxyhydrocarbyl; or R<sub>3</sub> and R<sub>4</sub> together and/or R<sub>5</sub> and R<sub>6</sub> together and/or R<sub>1</sub> and R<sub>3</sub> together and/or R<sub>2</sub> and R<sub>4</sub> together may form cyclic groups; and x is a number from 1 to about 8.

52. The composition of claim 51 wherein in Formula XVII, R<sub>5</sub> and R<sub>6</sub> are independently lower hydrocarbyl groups.

53. The composition of claim 51 wherein in Formula XVII, any two of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are hydrogen.

54. The composition of claim 51 wherein in Formula XVII, x is 1 to about 3.

55. The composition of claim 51 wherein in Formula XVII, R<sub>1</sub> and R<sub>2</sub> are hydrogen, and R<sub>3</sub> or R<sub>4</sub> is a hydrocarbyl group containing from 1 to about 100 carbon atoms.

56. The composition of claim 51 wherein in Formula XVII, R<sub>3</sub> or R<sub>4</sub> contains from 1 to about 30 carbon atoms.

57. The composition of claim 1 wherein x in Formula I is a number from 1 to about 4.

58. The composition of claim 1 wherein in Formula I, G<sub>1</sub> and G<sub>2</sub> are identical.

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59. The composition of claim 1 wherein in Formula I, R<sub>1</sub> and R<sub>3</sub> are H or hydrocarbyl groups and G<sub>1</sub> and G<sub>2</sub> are C(O)H.

60. The composition of claim 1 wherein in Formula I, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are hydrogen or hydrocarbyl groups, and both G<sub>1</sub> and G<sub>2</sub> are NO<sub>2</sub> groups.

61. The composition of claim 1 wherein in Formula I, G<sub>1</sub> and G<sub>2</sub> are C(X)R wherein R is a hydrocarbyl group.

62. The composition of claim 1 wherein in Formula I, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each independently hydrogen or hydrocarbyl groups and G<sub>1</sub> and G<sub>2</sub> are R<sup>5</sup>-C=NR<sup>6</sup> groups wherein R<sup>5</sup> and R<sup>6</sup> are each independently hydrogen, hydrocarbyl groups or the two R<sup>6</sup> groups together form a hydrocarbylene group joining the two nitrogen atoms.

63. The composition of claim 1 wherein in Formula I, R<sub>2</sub> and R<sub>4</sub> are hydrogen or hydrocarbyl groups and R<sub>1</sub>, R<sub>3</sub>, G<sub>1</sub> and G<sub>2</sub> are C(O)R wherein R is a hydrocarbyl group.

64. The composition of claim 1 wherein in Formula I, R<sub>2</sub> and R<sub>4</sub> are hydrogen or hydrocarbyl groups, R<sub>1</sub> and R<sub>3</sub> are COOR groups, and G<sub>1</sub> and G<sub>2</sub> are C(O)R groups wherein each R is hydrogen or a hydrocarbyl group.

65. The composition of claim 1 wherein in Formula I, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are H or lower hydrocarbyl groups containing from 1 to about 7 carbon atoms.

66. A composition comprising:

(A) at least one compound selected from the group consisting of magnesium sulfonate, sodium sulfon-

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ate, magnesium salicylate or a mixture of two or more thereof;

(B) at least one compound selected from the group consisting of benzotriazole, tolyltriazole or a mixture thereof;

(C) a mixture of

(C-1) at least one phosphorodithioic acid amide; and

(C-2) at least one phosphorodithioic acid ester.

67. A concentrate comprising from about 10% to about 90% by weight of the composition of claim 1 and a diluent.

68. A lubricant or functional fluid comprising a major amount of an oil and a minor amount of the composition of claim 1.

69. A concentrate made by combining components (A), (B) and (C) of claim 1 with a diluent, the combined weight of said components (A), (B) and (C) comprising from about 10% to about 90% by weight of said concentrate.

70. A lubricant or functional fluid made by combining minor amounts of components (A), (B) and (C) of claim 1 with a major amount of an oil.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>4</sup> :</b> <b>C10M 141/08, 141/10, 163/00</b>	<b>A3</b>	<b>(11) International Publication Number:</b> <b>WO 89/ 04358</b> <b>(43) International Publication Date:</b> 18 May 1989 (18.05.89)
<b>(21) International Application Number:</b> PCT/US88/03723 <b>(22) International Filing Date:</b> 21 October 1988 (21.10.88) <b>(31) Priority Application Number:</b> 117,254 <b>(32) Priority Date:</b> 5 November 1987 (05.11.87) <b>(33) Priority Country:</b> US <b>(71) Applicant:</b> THE LUBRIZOL CORPORATION [US/US]; 29400 Lakeland Boulevard, Wickliffe, OH 44092 (US). <b>(72) Inventors:</b> ADAMS, Paul, E. ; 35951 Maplegrove Road, Willoughby Hills, OH 44094 (US). VINCI, James, Noel ; 131 Chatham Way, Mayfield Heights, OH 44124 (US).		<b>(74) Agents:</b> TRITT, William, C. et al.; The Lubrizol Corporation, 29400 Lakeland Boulevard, Wickliffe, OH 44092 (US). <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent). <b>Published</b> <i>With international search report</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <b>(88) Date of publication of the international search report:</b> 24 August 1989 (24.08.89)
<b>(54) Title:</b> COMPOSITIONS AND LUBRICANTS AND FUNCTIONAL FLUIDS CONTAINING SAME <div style="text-align: center; margin: 20px 0;"> <math display="block">  \begin{array}{c}  R^1 \\    \\  G^1 - C - (S)_x - C - G^2 \\    \qquad \qquad   \\  R^2 \qquad \qquad R^4  \end{array}  \qquad (I)  </math> </div> <b>(57) Abstract</b> <p>A composition is disclosed which comprises: (A) at least one neutral or basic metal salt or boron-containing neutral or basic metal salt of at least one acidic organic compound, the metal in said salt being selected from the group consisting of alkali metals, alkaline-earth metals, zinc, copper, aluminum or a mixture of two or more of said metals; (B) at least one metal deactivator; and (C) at least one compound selected from the group consisting of (C-1) phosphorus-containing amide; (C-2) phosphorus-containing ester; (C-3) sulfur-coupled dithiocarbamate; (C-4) sulfur-containing compound represented by the formula (I), wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each independently H or hydrocarbyl groups, R<sup>1</sup> and/or R<sup>3</sup> may be G<sup>1</sup> or G<sup>2</sup>; R<sup>1</sup> and R<sup>2</sup> and/or R<sup>3</sup> and R<sup>4</sup> together may be alkylene groups containing about 4 to about 7 carbon atoms; G<sup>1</sup> and G<sup>2</sup> are each independently C(X)R, COOR, C≡N, R<sup>5</sup>-C=NR<sup>6</sup>, CON(R)<sub>2</sub> or NO<sub>2</sub>, and G<sup>1</sup> also may be CH<sub>2</sub>OH, wherein X is O or S, each of R and R<sup>5</sup> are independently H or a hydrocarbyl group, R<sup>6</sup> is H or a hydrocarbyl group; when both G<sup>1</sup> and G<sup>2</sup> are R<sup>5</sup>C=NR<sup>6</sup>, the two R<sup>6</sup> groups together may be a hydrocarbylene group linking the two nitrogen atoms; when G<sup>1</sup> is CH<sub>2</sub>OH and G<sup>2</sup> is COOR, a lactone may be formed by intramolecular condensation of G<sup>1</sup> and G<sup>2</sup>; and x is an integer from 1 to about 8; and (C-5) mixture of two or more of any of (C-1) to (C-4). These compositions are useful as additives for lubricants and functional fluids, particularly hydraulic fluids, gear oils, greases and the like.</p>		

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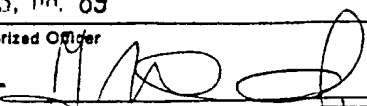
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RO Romania  
SD Sudan  
SE Sweden  
SN Senegal  
SU Soviet Union  
TD Chad  
TG Togo  
US United States of America

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 88/03723

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> : C 10 M 141/08, C 10 M 141/10, C 10 M 163/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	C 10 M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT*</b>		
Category *	Citation of Document, <sup>11</sup> with Indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 3923669 (T.D. NEWINGHAM) 2 December 1975 see abstract; column 2, lines 13-56; column 4, line 23 - column 6, line 46; example; column 7, line 41 - table VI; claims 1,3-5 --	1,2,67-70
X	DE, A, 2162180 (EDWIN COOPER & CO. LTD) 6 July 1972 see page 2, line 5 - page 3, line 13; page 4, line 1 - page 5, line 4; page 5, lines 8-13,15-26; page 6, lines 11-18; example 1,2; claims 1-4,9,11,12 --	1-4,9-11, 67-70
X,L	US, A, 4466894 (K.B. GROVER) 21 August 1984 see abstract; column 1, line 9 - column 7, line 62; column 12, line 12 - column 15, line 15; column 17, lines 9,10,12,18-28,30-65; claims 1-10,14,15,22-26,28,30,32,33 cited in the application ./. --	1-5,67-70
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
27th June 1989		03.08.89
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		M. VAN MOL 

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	--	6-11
Y,L	US, A, 4100082 (D.L. CLASON et al.) 11 July 1978 see abstract; column 12, line 10 - column 16, line 41; column 25, line 48 - column 26, line 4; column 27, lines 4-13,18-20; claim 1 cited in the application	6-11
A	--	2-5
X,L	WO, A, 86/06092 (THE LUBRIZOL CORP.) 23 October 1986 see page 1, line 5 - page 3, line 28; page 18, line 27 - page 19, line 24; page 21, line 8 - page 23, line 7; page 64, line 16 - page 78, line 15; page 80, line 17 - page 81, line 27; page 85, lines 22-32; examples V, X, XI; page 90, lines 3-15; claims 7-14,19-26,41-48,57	1,2,67-70
Y	--	3-11
Y,L	US, A, 4200545 (D.L. CLASON et al.) 29 April 1980 see column 1, lines 7-56; column 12, lines 42-66; column 14, line 42 - column 16, line 66; column 25, line 44 - column 26, line 29	3-11
A	--	2
Y,L	US, A, 4627928 (J.L. KARN) 9 December 1986 see abstract; column 1, lines 16-55; column 2, lines 23-61; column 3, line 12 - column 8, line 47; column 9, line 29 - column 10, line 64; column 19, line 36 - column 21, line 41; claims 1,2,4,6,8,9,19, 21-25,30,32,34,37,39,42,44 cited in the application	7-11
X	US, A, 3923669 (T.D. NEWINGHAM) 2 December 1975 see abstract; column 2, lines 13-56; column 4, line 23 - column 6, line 40; example; column 7 - table V; claim 1	29,30
Y	--	31
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages.	Relevant to Claim No
X	US, A, 4181619 (R.H. SCHMITT et al.) 1 January 1980 see abstract; column 1, line 6 - column 2, line 55; column 3, lines 4-48; examples; claims 1-3,6-10	29,30
X,L	GB, A, 2071139 (THE LUBRIZOL CORP.) 16 September 1981 see abstract; page 1, lines 6-62; page 7, line 12 - page 10, line 67; page 11, lines 2-37; claims 1-4,6,11,13,14	29-31
A	US, A, 4119549 (K.E. DAVIS) 10 October 1978 see abstract; column 1, line 65 - column 2, line 55; table II, examples 30,31; column 7, lines 23-39; column 9, lines 4-49; column 10, line 48 - column 11, line 14; examples K,L	
X,L	CA, A, 1168222 (THE LUBRIZOL CORP.) 29 May 1984 see page 1, line 3 - page 2, line 33; page 22, line 7 - page 25, line 16; page 26, lines 24,25,33 - page 27, line 15; page 30, line 4 - page 31, line 11; page 32, line 28 - page 33, line 31; claims 1-4,7,9,13,14 cited in the application	29-31
X,L	US, A, 4466894 (K.B. GROVER) 21 August 1984 see abstract; column 1, line 9 - column 5, line 7; column 6, line 35 - column 8, line 14; column 12, line 39 - column 13, line 40; column 15, lines 9-53; column 17, lines 9-60; claims 1,2,13,14,19-26, 32,33	29-31
P,X, L	WO, A, 88/03554 (THE LUBRIZOL CORP.) 19 May 1988 see abstract; page 1, line 4 - page 19, line 22; page 28, line 29 - page 33, line 4; page 34, line 27 - page 38, line 4; page 77, line 31 - page 80, line 3; page 82, lines 1-4; page 93, line 3 - page 94, line 2; page 96, line 32 - page 99, line 2; ./.	29-31

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

page 100, line 30 - page 101, line  
26; page 104, lines 1-35; claims  
1-28, 34, 52-63  
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V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ..... because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers ..... because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>2</sup>

This international Searching Authority found multiple inventions in this international application as follows:

Please see Form PCT/ISA/206 of 04-04-89

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims: 1-11, 67-70  
29-31

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the international Searching Authority did not invite payment of any additional fee.

Remark on Protest

☒ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8803723  
SA 25400

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 27/07/89  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3923669	02-12-75	BE-A- 835042	30-04-76
		CA-A- 1063590	02-10-79
		DE-A- 2547793	06-05-76
		FR-A- 2289600	28-05-76
		JP-A- 51065104	05-06-76
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